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# USSR Report

CHEMISTRY

No. 72

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3 October 1980

## USSR REPORT

## CHEMISTRY

No. 72

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## CHEMICAL INDUSTRY

### HIGH STATE COMMISSIONS NOTE MINISTRY SHORTFALLS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 31 May 80 p 1

[Article: "To Perfect Chemical Production. In the USSR Supreme Soviet Chambers Commissions"]

[Text] On 30 May, a joint session of the commissions on industry of the USSR Supreme Soviet's two chambers, the Soviet of the Union and the Soviet of Nationalities, was held in the Kremlin. The question of fulfillment of state plan tasks by the USSR Ministry of the Chemical Industry and recommendations of the permanent commissions of the USSR Supreme Soviet chambers regarding the expansion of production of the most important types of chemical products were discussed.

The fact that during last the last 20 years the chemical industry developed at outstripping rates was noted in the deputies' reports and addresses. During this time interval, the volume of output of the chemical and petrochemical industry rose by a factor of 7.8. In just the preceding two five-year plan periods, the production of mineral fertilizers almost tripled, and the Soviet Union advanced to first place in the world in terms of total fertilizer output. The production of synthetic resins and plastics during this time rose by a factor of 3.5, and the output of chemical fibers and thread increased by a factor of almost 2.3. The volume of output of other types of products also grew considerably.

It was also noted that in managing the industry the USSR Ministry of the Chemical Industry, although achieving specific successes, nevertheless, had not ensured in full measure the practical realization of the course proclaimed by the 25th CPSU Congress regarding the multifaceted increase in the efficiency of production, regarding acceleration in the rates of technical progress, and regarding improvement in the satisfaction of the national economy needs for industrial goods; and it did not take all necessary measures to implement the broad program for the development of the chemical industry.

The adopted decision included recommendations for the elimination of the exposed shortcomings and for a more complete utilization of existing capacities.

Candidate Member of the CC CPSU Politburo, First Deputy Chairman of the Presidium of the USSR Supreme Soviet V.V. Kuznetsov took part in the work of the session.

[206-P]

CSO: 1841

## LARGE ISOPRENE COMPLEX BUILT

Moscow IZVESTIYA in Russian 18 May 80 p 1

[Article by E. Kondratov: "Front Page Story: Volga Isoprene"]

[Text] Novokuybyshevsk. The first thousands of tons of isoprene have been obtained at the Novokuybyshevsk Petrochemical Combine imeni 50-letiya SSSR.

Several weeks ago, I would have had to write this story from the construction site; now, however, the second stage of the combine -- a large complex of 39 facilities and shops -- is in operation. A huge volume of work was performed by construction and installation workers of Trust No 25 and by many subcontractor organizations. On the hundred hectares occupied by the complex for the production of isoprene, more than 350,000 cubic meters of reinforced concrete were laid, more than 400 kilometers of electric power cables were strung, about 10,000 tons of metal structures were erected, and more than 1,000 kilometers of technological pipelines were installed.

Start-up of the new production facility signified essentially the birth of a large modern plant furnished with the latest equipment and distinguished by better technology than at similar enterprises.

The new complex quickly fell into its working pace. Tank car after tank car loaded with isoprene, a colorless liquified gas, departs the loading platform for Nizhnekamsk and Tol'yatti to be processed into synthetic rubber, which is not only as good as but in some respects is even better than natural rubber. The product from Novokuybyshevsk has a very important significance for many sectors of the national economy -- for good rubber is literally needed everywhere.

"For it to be really good," emphasized the combine's Director G. Vasil'yev, with whom we inspected the shops of the new complex, "it is essential that the isoprene be absolutely pure. This is why that at all technological transfer operations special attention is paid to product quality."

Separation of isoprene from crude, the so called unstable gasoline, is a multistage process requiring extreme precision in the operation of all links in the technological chain. High precision equipment is operating at the new complex; equipment which Novokuybyshev personnel were taught to use in Sungait, Sterlitamak, Voronezh and Kazan'.

In the operational room of shop IR-6 -- and it is precisely in this shop that the final product is obtained -- R. Rodionov's work shift confidently conducted the technological process. The young operators worked the complicated equipment as if they had used it for many years.

"We are pleased that right from the start we obtained isoprene of good quality," declared G. Vasil'yev, "but as far as the complex beginning to operate at its designed capacity, we will try to achieve this several months ahead of schedule."

[205-P]

CSO: 1841

## LARGEST ETHYLENE OXIDE PRODUCTION FACILITY BUILT

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 4 May 80 p 1

[Article by N. Sorokin: "Shock Speeds of the Petrochemists"]

[Text] Nizhnekansk, Tatarskaya ASSR. The largest domestic ethylene oxide production facility has been put into operation at the Nizhnekansk "Nizhnekanskneftekhim" Petrochemical Association. Initial shipments of the product used as the valuable basic ingredient in the production of plastics, synthetic fibers, cleansing agents and paints have been sent today to user plants.

This achievement is the Nizhnekansk people's answer to L. I. Brezhnev's greeting to the participants in the construction and the start-up of the complex for the production of isoprene rubber. The production of ethylene oxide was organized in short periods of time. Construction, installation and start-up work were done on an integrated schedule.

I. Mikhaylov's crew from the "Dvigatel'montazh" (Motor Installation) Trust spearheaded the socialist competition among the collectives of the 20 contract organizations. The use of the brigade contract method made possible the installation of the very high power compressors in half the normal time.

Putting the ethylene oxide complex into operation is a new step in the automation of petrochemical enterprises. The "Tsentr" (Center) automated control system, permitting a one-third reduction in the number of service personnel was installed here.

The Nizhnekansk Petrochemical Complex is growing at fast rates. Since the beginning of the quinquennium, 12 production facilities were created here; and, before the end of 1980, three more will be put into operation. [197-P]

CSO: 1841

PHOTOGRAPH SHOWS TOBOL'SK PETROCHEMICAL STORAGE FACILITY

Moscow BOTRIALISTICHESKAYA INDUSTRIYA in Russian 11 Jul 80 p 1

[Article: "Petrochemical Giant Under Construction"]

[Excerpt] Construction and installation workers of the Tobol'sk Petrochemical Combine have obligated themselves to put the first stage of the enterprise into operation by the end of July. At present, start-up operations and run-in and testing of equipment is under way at the propane storage facility, at the pouring and filling trestle, and at other structures.



The photograph shows the storage facility for finished products.  
[221-P]

CSO: 1841

#### BRIEFS

**NEW PETROCHEMICAL COMBINE**--The fourth-lift water-pump station, which is the first industrial facility of the stage now under construction at the Tomsk Petrochemical Combine, is ready for operation. The station will supply the enterprise with more than 6,000 cubic meters per day of industrial and drinking water. Preparations are under way for the start-up of ten more facilities in the first stage for the production of polypropylene. Set-up workers from Installation Administration No 70 of the "Khimelektromontazh" Chemical and Electrical Installation Trust are now working both rapidly and well on the first lowering substation in the three shops of the main production facility. Purification facilities and nitrogen-oxygen and hydrogen stations are near full readiness. The tight schedules for putting the facilities on line demand both initiative and responsibility from each participant in the construction. Thus, the drivers of the transportation shop of the combine learned how to move large heavy equipment. Whereas a 40-ton load was their limit previously, they have now delivered to the lowering substation a 150-ton transformer. Drivers N. Makarov, V. Matusevich and V. Kashtonov accomplished this on a complicated route with bad and difficult roads. [Text] [Moscow EKONOMICHESKAYA GAZETA in Russian No 26, Jun 80 p 9] [217-P]

**BUTYL ALCOHOL COMPLEX**--Salavat. G. Kikman. The first stage of a complex for the production of 85,000 tons of butyl alcohol annually has been put into operation at the Salavat Petrochemical Combine. Ammonia, carbamide, ethylene oxides, and polyethelene are the other products of the combine which are well known to field-crop growers and to chemists. The product mix has now been augmented to include components which are needed in the production of rubber, caoutchouc and articles made from them. All of the presently operating facilities have been installed by workers of the Order of the October Revolution Trust "Vostokneftezavodmontazh" (Eastern Petroleum Refinery Installation Trust). [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 7 Jul 80 p 1] [204-P]

**KRASNODAR CHEMICAL PLANT**--Krasnodar. The Krasnodar "KRASNODARKHIMSTROY" Chemical Construction Trust is building the Krasnodar Chemical Plant for the production of complex mineral fertilizer near the young Kuban' city of Belorechensk. Already 2 years have passed since sulfuric acid production has reached designed capacity; and recently, the facility for the production of complex liquid fertilizers has been fully put on stream. These fertilizers are the most efficacious of all existing types and possess all essential components for the life of plants. [Text] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 2 Jun 80 p 2] [218-P]

**LARGE DIAMETER PLASTIC PIPE**--The largest USSR polyethylene pipe plant has begun operating at the Kazan' Organic Synthesis Production Association. All operations are automated at the new enterprise. Its annual capacity is 30,000 tons of pipe with diameters from 63 to 1,200 millimeters. Polymer stock, derived from natural gas, is one eighth the weight of steel. Heavy equipment is not required to move and to install this pipe; besides, polyethylene is not subject to corrosion and is immune to freezing temperatures and caustic media. [Text] [Moscow IZVESTIYA in Russian 18 May 80 p 1] [198-P]

**LARGEST ETHYLENE OXIDE PLANT**--The largest USSR facility for the production of ethylene oxide has been put on line at the Nizhnekamsk "Nizhnekamsk-neftekhim" Petrochemical Association. The Nizhnekamsk Petrochemical Complex is growing rapidly. Since the beginning of the quinquennium, twelve production facilities have been built; by the end of the year, three more will be put into operation. [Text] [Moscow EKONOMICHESKAYA GAZETA in Russian No 19, May 80 p 3] [203-P]

**SULFURIC ACID OUTPUT TO GROW**--Grodno. The "Azot" Association imeni S. O. Pritytskiy will provide sulfuric acid not only for its own increased needs but also for those of other USSR enterprises. After reconstruction, the complex, designed for the annual production of 120,000 tons of this valuable component in the output of mineral fertilizer, has already started making the product. The chemists have obligated themselves to put the facility on stream and to attain the planned goals by the sixty-third anniversary of the Great October, i.e., twice as fast as the norm. [Excerpt] [Moscow SOTSIALISTICHESKAYA GAZETA in Russian 4 Jul 80 p 1] [219-P]

**NEW AMMONIA FACILITY ON LINE**--Before the beginning of the new year, a large ammonia production complex at the Dorogobuzh Nitrogen Fertilizer Plant was put on line. It is capable of producing 450,000 tons of ammonia, 380,000 tons of diluted nitric acid and 765,000 tons of ammonium nitrate annually. [Excerpt] [Moscow EKONOMICHESKAYA GAZETA in Russian No 2, Jan 80 p 3] [199-F]

FERTILIZER PRODUCTION--Kingsnapp. Since 1 January 1980, the output of the "Fosforit" Association totaled hundreds of thousands of rubles have the plan, including more than 5,000 tons of ammophos and about 100,000 tons of phosphate fertilizer. Before the end of 1980, the additional output will total 500,000 rubles worth and will include 3,000 tons of phosphate fertilizer and 150 tons of highly pure sulfuric acid. [Excerpt] [Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 15 Jul 80 p 1] [220-P]

LATVIAN FERTILIZER PRODUCTION--Ye. Vostrukhov. The Ventspils Port Plant, the largest chemical enterprise in the Baltic area, has begun the production of a new product, ammonium hydroxide. The first lot of the valuable nitrogen fertilizers has already been sent from here to Latvian farms. Before the end of the second quarter, 10,000 tons of ammonium hydroxide will be shipped. Construction at the plant continues: new facilities are being built, railroad sidings are being laid and platforms are being constructed. An intricate complex of purification equipment has been recently put into operation. [Text] [Moscow IZVESTIYA in Russian 3 Jul 80 p 2] [202-P]

FERTILIZER PRODUCTION DOUBLES--After radical reconstruction, the second stage of the ammophos complex at the chemical plant in Kedainiai, Lithuanian SSR, has produced its first product. Production capacity has doubled as the result of technical reequipping. Some 340,000 tons of concentrated fertilizers will now be produced annually. [Text] [Moscow EKONOMICHESKAYA GAZETA in Russian No 17, Apr 80 p 4] [201-P]

KUYBYSHEV FERTILIZER--The third ammonia unit with a 450,000-ton annual fertilizer production capacity has been put into operation at the Kuybyshev "Kuybyshevazot" Nitrogen Association. In 1979, construction workers of the Kuybyshev "Kuybyshevgidrostroy" [Hydraulic Structures] Construction Trust have put on stream three ammonia units with a total annual capacity of 1,350,000 tons and a carbamide unit with an annual capacity of 480,000 tons. [Text] [Moscow EKONOMICHESKAYA GAZETA in Russian No 2, Jan 80 p 3] [200-P]

UDC 66.094.37:[661.7.547.271:261]  
661.727.1

TEST OF A PILOT FACILITY FOR THE PRODUCTION OF FORMALDEHYDE BY OXIDIZING  
DIMETHYL ETHER

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 6, 1980 pp 333-335

GERTSEN, P. P., ROZHKOV, V. S., BASHMAKOV, I. V., SOLOMONOV, A. B., NAUMOV, V. M., MAL'TSEVA, A. A., SKUDAYEV, V. I., MOROZOVSKIY, A. I., IONOVA, L. I., and SHUMIKHIN, A. G.

[Abstract] Dimethyl ether (DME) is the principal byproduct of methanol synthesis. To utilize this byproduct, the Perm' Polytechnical Institute and Gubakhin Chemical Plant have proposed a method for selective fluidized bed catalytic oxidation of DME into formaldehyde. To this end, a pilot production facility handling about 200 kg DME daily has been built. Operating trials of this facility showed that the optimal selectiveness of the process, 75-78%, is achieved at 580-610°C. Highly concentrated gases can be passed through the fluidized bed catalyst without danger of explosion, the reaction mixture of DME and air being passed across the heated catalyst. The experimental findings have been used to construct an improved kinetic model of the reactor with a fixed adiabatic layer of catalyst and, on this basis, a mathematical model of a four-shelf reactor with cooling of reaction gases following each stage. Figures 3; references 4: 3 Russian, 1 Western. [209-1386]

UDC 66.097.322:[66.094.3:661.715.24]

TESTS OF AN IRON-TELLURIUM-MOLYBDENUM CATALYST FOR THE OXIDATION OF ISO-  
BUTYLENE INTO METHACROLEIN

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 6, 1980 pp 335-337

FEDEVICH, Ye. V., KRYLOVA, V. V., ZHIZNEVSKIY, V. M., GROBOVA, K. I. and SEMENOVA, V. A.

[Abstract] The possibility of oxidizing isobutylene into methacrolein with the aid of an iron-tellurium-molybdenum catalyst to maximize the conversion of the original olefin was investigated. The atomic ratio among the active components of the catalyst was Fe:Te:Mo = 1:0.85:1. The catalyst was prepared in the form of 3-5 mm grains with crushed quartz or porcelain in the same particle size as the inert diluent. Laboratory tests showed that when this catalyst is used the oxidation of isobutylene in the form of an

isobutylene-air mixture containing 5 vol.% of isobutylene results in nearly total conversion of olefin, with the selectiveness with respect to methacrolein amounting to 77-81%. Since explosive isobutylene-air mixtures cannot be oxidized on an industrial scale, experiments with the oxidation of mixtures containing 1.9 vol.% isobutylene were conducted, and also were successful. References 6: 5 Russian, 1 Western.  
[209-1386]

UDC 66.095.253.7:[661.7:547.532]:661.715.333

#### SYNTHESIS OF ISOPROPYLBENZENE WITH THE AID OF PHOSPHORIC ACID CATALYST

Moscow KHEMICHESKAYA PROMYSHLENNOST' in Russian No 6, 1980 pp 339-340

PAVLOV, G. P., KAZAKOV, Yu. M., KORNEYEVA, O. V., SINOVIKH, I. D., ZAVOROTOV, V. I., KRAMAR, A. Ya., BORMOTOV, A. I. and KHABLO, I. I.

[Abstract] The possibility of using phosphoric acid as a catalyst for the alkylation of benzene with propylene in the production of isopropylbenzene was experimentally investigated. The alkylation was performed in the presence of shaped phosphoric acid catalyst--polyphosphoric acid on silicagel ( $P_2O_5$  content--60-65%). Mathematical and statistical analysis of the findings showed that the optimal parameters of the alkylation are: volume flow rate of reaction mixture,  $4.2 \text{ hr}^{-1}$ ; molar ratio between benzene and propylene, 5-6; reactor temperature,  $230^\circ\text{C}$ . Under these conditions isopropylbenzene yield is 680 g(liter-hr). There was no decrease in the activity of the phosphoric acid catalyst during the entire experimental run of 1200 hr, and the isopropylbenzene thus produced satisfied the quality standards. Figures 2; references 8: 7 Russian, 1 Western.  
[209-1386]

UDC 661.7:547.638.66.097.3.661.183.123.2

#### NEW METHOD FOR THE PRODUCTION OF DIPHENYLOLPROPANE

Moscow NEFTEPERERABOTKA I NEFTEKHIMIYA in Russian No 11, 1979 pp 34-35

VERKHOVSKAYA, Z. N., MESHCHERYAKOV, S. T., DAROVSEKIKH, I. F., et al, All-Union Scientific Research Institute of Organic Synthesis

[Abstract] In 1978 a new production plant for diphenylolpropane (2,2-bis-(4'-hydroxyphenyl)propane) (I) was opened. The new production method was based on the condensation of phenol with acetone in presence of solid catalysts: strongly acidic cations containing sulfogroups and promoters. When an excess of phenol is used at 55-75°C, an acetone can be quantitatively converted to I. Among the advantages of the new method are the following: one year performance period of the catalyst, easy isolation of products in highly pure state, low production waste and absence of strong aggressive media. Figure 1; no references.

[151-7813]

UDC 665.642-986.661.715.33(47+57)658.012.12.65.011.46

#### PRINCIPAL DIRECTIONS FOR INCREASED EFFECTIVENESS IN THE PRODUCTION OF ETHYLENE IN THE USSR

Moscow NEFTEPERERABOTKA I NEFTEKHIMIYA in Russian No 11, 1979 pp 27-29

MUKHINA, T. N., AVREKH, G. L. and SHESTAKOVA, L. M., et al, All-Union Scientific Research Institute of Organic Synthesis

[Abstract] Currently, the production of lower olefines, based on pyrolysis of hydrocarbons, represents one of the basic sources of starting materials in organic synthesis. An 8-9 percent growth of the production of olefines has been observed both in the USSR and abroad. To satisfy the increased production requirements, a series of plant expansions has been initiated and a search for new starting materials is under way. Among the specific measures proposed are the following: conversion of the equipment to high temperature pyrolysis, inhibition of coke deposits in pyrolytic ovens, use of special process initiators, introduction of new equipment such as EP-300 designed for large scale production, etc. With the introduction of this equipment, attention will be paid to the recovery of by-products--benzene, toluene, xylene--as a cost saving measure. Finally, serious consideration is given to possible use of gas-oil as the starting material. No references.

[151-7813]

## UTILIZATION OF SECONDARY RESOURCES OF ENERGY

Moscow NEFTEPERERABOTKA I NEFTEKHIMIYA in Russian No 11, 1979 pp 38-39

ZIZYUKIN, V. K. and ZELENTSOVA, N. I., All-Union Scientific Research Institute of Organic Synthesis

[Abstract] Large production plants of ethylene require considerable cooling for the separation of the gases obtained during pyrolysis. Normally special compressors are constructed at the site, however it has been proposed that brom-lithium absorption-cooling machines (ACM) be used. These machines could be operated on the normally wasted heat source--the pyrogas stream mixed with steam emitted from the top of primary fractionation column. ACM could produce a cooling source at a rate of 125 kcal/hr. To achieve adequate cooling capacity by means of this secondary energy source, several ACM's must be utilized. In addition, ACM's with higher kcal/hr efficiency must be developed. No references.  
[151-7813]

## DIRECTION FOR FURTHER DEVELOPMENT OF THE PRODUCTION OF SYNTHETIC ETHANOL

Moscow NEFTEPERERABOTKA I NEFTEKHIMIYA in Russian No 11, 1979 pp 36-38

BOUDEN, B. S., POZIN, L. S., VERKHOVSKAYA, Z. N., et al, All-Union Scientific Research Institute of Organic Synthesis

[Abstract] Currently 60 percent of the ethanol produced in the USSR is used for synthesis of divinyl. Ethanol is also required for microbiological synthesis of proteins. The existing plants must be modified to assure sufficiently high productivity of synthetic ethanol. Research at the All-Union Scientific Research Institute of Organic Synthesis concentrates on development of new technology for production, on purification methods and development of new syntheses. A mathematical and an economical model are being developed for the performance of vapor phase hydration reactor, and for the evaluation of cost effectiveness. Attention is directed towards the basic theory of film type catalysts; quantitative relationships were found between the productivity of a catalyst, the structure of the carrier and its content of phosphoric acid. The results from mathematical model led to modification of the technical processes. Economical models suggested reconstruction of the existing, and construction of new plants. No references.  
[151-7813]

THE STATUS AND TECHNICAL PROGRESS OF THE PRODUCTION OF ACETALDEHYDE IN THE USSR

Moscow NEFTEPERERABOTKA I NEFTEKHIMIYA in Russian No 11, 1979 pp 40-41

LANGE, S. A., and KHCHEYAN, Kh. Ye., All-Union Scientific Research Institute of Organic Synthesis

[Abstract] Acetaldehyde is one of the more important intermediates in organic synthesis. In 1970 a plant was opened in the USSR for production of acetaldehyde through direct oxidation of ethylene in presence of aqueous solutions of palladium and copper salts. In the common two-stage method of ethylene oxidation considerable volume of chloroorganic byproducts is produced resulting from the presence of copper chloride. A new catalyst and a new oxidation process were developed at the All-Union Scientific Research Institute of Organic Synthesis. The catalyst is considerably more active and less expensive than any other catalyst in existence. The chlorination reaction is reduced considerably with the use of this new catalyst. Oxidation of ethylene with oxygen lowers the production of chlorinated and polymerized by-products while increasing somewhat the yield of acetaldehyde. Reference: 1 Western.  
[151-7813]

## NEW METHODS OF IMMOBILIZING NUCLEOSIDES

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 1, 1980 pp 134-135  
manuscript received 5 Oct 79

MITINA, V. Kh., KLYASHCHITSKIY, B. A., DUBININA, I. G. and VORNOVITSKAYA, G. I., USSR Academy of Medical Sciences Institute of Biological and Medical Chemistry, Moscow, and USSR Academy of Medical Sciences Oncological Science Center, Moscow

[Abstract] Several new approaches to the immobilization of nucleosides on solid carriers are discussed. For the purpose of attaching uridine to "Sefarose" at the 5'-position, 2',3'-O-isopropylidene uridine was oxidized according to the Pfitzner-Moffatt method (1963) and the product produced was hydrolyzed with aqueous acetic acid for 2 h at 100°C. The uridine-5'-aldehyde separated was attached without purification to glutaryl hydrazide or adipinyl hydrazide "Sefarose" with a pH of 5 for 2 h at 20°C, which resulted in individual derivatives I and II. The data of a spectrophotometric determination showed that about 9  $\mu$ moles of uridine per ml of gel were bound to the "Sefarose." According to another method, azauridine was converted into 5'-carboxymethyl azauridine, which was condensed with amino ethyl or amino hexyl "Sefarose" by means of 1-ethyl-3-(3-dimethyl amino propyl) carbodiimide or by means of a mixed anhydride, and two other derivatives, III and IV, respectively, were produced. The content of azauridine in III and IV equaled 3 to 5  $\mu$ moles per ml of gel. An adsorbent (V) was produced which contained 5.5  $\mu$ moles of uridine per ml of "Sefarose." This latter experiment demonstrated that the incubation of uridine with epoxy-activated "Sefarose 6V" for 16 h at 37°C in 0.1 M NaOH results in the covalent bonding of the nucleoside to "Sefarose." A periodate-oxidized nucleoside was condensed with bovine serum albumin (BSA) for the purpose of immobilizing ribonucleosides through the ribose section by means of a polymeric protein insertion. The dissolved complex produced was attached to "Sefarose 4V" activated with CNBr. Thus were produced "uridine-BSA-'Sefarose'" and "thioguanosine-BSA-'Sefarose.'" References 3: 1 Russian, 2 Western.  
[145-8831]

IMMOBILIZATION OF A PROTEASE FROM *BACILLUS MENTERICUS* ON SILOCHROMES

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 1, 1980 pp 104-109  
manuscript received 18 Oct 79

DAVIDENKO, T. I., CHUYENKO, A. V. and BONDARCHUK, A. A., Ukrainian SSR  
Academy of Sciences Physical Chemistry Institute, Odessa, and Ukrainian SSR  
Academy of Sciences Institute of Microbiology, Kiev

[Abstract] Methods are described for producing proteases of *Bacillus mesentericus* immobilized on silochromes by means of various crosslinking reagents, such as cyanur chloride, 2,4-toluylene diisocyanate, glutaraldehyde, thionyl chloride, phosphorus tribromide, titanium tetrachloride, and zirconium oxychloride and hafnium oxychloride. The selection of carriers was governed by such factors as accessibility, low cost and the possibility of considering carriers both with various reaction groups remote from the surface of the silochrome and directly linked to the carriers. An example of the former is chlorotriazine, diisocyanate and aldehyde groups, and of the latter, chlorine- and bromine-containing groups and silochromes modified by salts of transition metals. The specific content of enzyme per gram of carrier depends on the method of immobilization and varies from 71.5 mg of protein for glutaraldehyde to 125.1 for 2,4-toluylene diisocyanate. The method of immobilization influences the activity of the preparations produced to an even greater degree: The highest percentage of preservation of caseinolytic activity is observed when using glutaraldehyde, thionyl chloride and salts of transition metals. A table is shown of the properties of the protease immobilized on silochromes in relation to the method of immobilization or the reagent. Properties considered are the amount of immobilized protein in ml/g of the carrier, the degree of bonding of the protein and the preservation of caseinolytic activity. In holding immobilized preparations of protease at 4°C for 10, 30 and 38 24-h periods, the activity of the enzyme changed curiously for different crosslinking reagents. Most stable were preparations produced by using cyanur chloride, glutaraldehyde and phosphorus tribromide (60 percent of the original activity preserved after 38 24-h periods) and hafnium oxychloride (68 percent after 30 24-h periods). A study of temperature inactivation demonstrated that at 70°C in the majority of cases the total inactivation of immobilized and native forms of the protease is observed. A description is given of the methods for producing a silochrome activated with thionyl chloride, a silochrome activated with phosphorus tribromide, a silochrome activated with salts of transition metals, and an immobilized protease of *Bacillus mesentericus*. In the latter case, to 15 to 20 mg of the enzyme in 2 ml of a tris-HCl buffer containing 0.005 M  $\text{CaCl}_2$  with a pH of 7.4 was added an activated carrier in a ratio of 136 mg of enzyme to 1 g of the carrier. The reaction mixture was incubated for 30 min at 25°C while shaking and was rinsed with a cooled tris-HCl

buffer with a pH of 7.4 to the point of the absence of absorption at 280 nm in the rinsing water. The preparation of the immobilized enzyme produced was stored in a tris-HCl buffer at 5°C in a refrigerator. The relationship between the activity of the immobilized protease and the temperature was determined by holding the immobilized protease in the tris-HCl buffer for 15 min at 30 to 70°C, cooling it in a beaker with ice and then determining the caseinolytic activity. In the control experiment, activity was determined without heating. Also described are the methods of determining the change in caseinolytic activity during multiple use and of determining the caseinolytic activity during storage. Figures 1; references 11: 10 Russian, 1 Western.  
[145-8831]

UDC 615.35:547.96].03(048.8)

PRESENT SITUATION AND PROSPECTS FOR USE IN MEDICINE OF IMMOBILIZED PHYSIOLOGICALLY ACTIVE SUBSTANCES OF PROTEIN NATURE (A REVIEW)

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 4, 1980 submitted 19 Sep 79, signed to press 27 Mar 80 pp 21-36

LARIONOVA, N. I. and TORCHILIN, V. P., Moscow University Laboratory of Molecular Biology and Bioorganic Chemistry, Academy of Medical Sciences All-Union Cardiological Center, Moscow

[Abstract] This review of the literature on the biomedical use of immobilized physiologically active substances of a protein nature discusses materials published after 1974. Areas of emphasis include: water soluble preparations of immobilized physiologically active substances, incorporation of protein medicines into liposomes, problems and prospects of directed transport of medicines in the organism, biodegraded preparations of immobilized proteins and the use in medicine of reactors with immobilized proteins. References: 178.  
[183-2791]

ARGININE IN THE ACTIVE CENTER OF PHOSPHOLIPASE A<sub>2</sub> FROM COBRA VENOM

Moscow BIOORGANICHESKAYA KHIMIYA in Russian Vol 6, No 5, 1980 pp 773-779  
manuscript received 19 Oct 79

APSALON, U. R. and MIROSHNIKOV, A. I., Moscow, Institute of Bioorganic Chemistry imeni M. M. Shemyakina, USSR Academy of Sciences

[Abstract] The possibility of detecting and pinpointing the site of the anion binding center of phospholipase A<sub>2</sub> isolated from the venom of the Central Asian cobra *Naja naja oxiana* was investigated. To this end, a chemical modification (isoenzyme E3) cobra-venom phospholipase A<sub>2</sub> was produced with 1,2-cyclohexanedione or acetylacetone. It was established that that enzyme contains a functionally important arginine residue responsible for bonding to the substrate molecule. It was also found that the functionally important arginine residue is located in the 16th position of the polypeptide chain. Modification with 1,2-cyclohexanedione results in a marked loss of activity as reflected in the presence of borate ions, which indicates that the modifiable arginine-16 residue participates in bonding the negatively charged phosphate group of the substrate molecule. These findings are of interest in view of the recently demonstrated importance of the phosphate or other negatively charged group in the substrate molecule to pancreatic phospholipase A<sub>2</sub>. Such a specificity presupposes the existence in the protein molecule of an anion-binding sector bearing a positive charge. References 29: 22 Russian, 7 Western.  
[181-1386]

## INTERACTION OF PHOTOREACTIVE DERIVATIVE OF THE NEUROTOXIN FROM THE CENTRAL ASIAN SCORPION VENOM AND NEUROBLASTOMA CELL MEMBRANES

Moscow BIOORGANICHESKAYA KHIMIYA in Russian Vol 6, No 5, 1980 pp 724-730  
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GRISHIN, Ye. V., SOLDATOV, N. M., OVCHINNIKOV, Yu. A., MOZHAYEVA, G. N., NAUMOV, A. P., ZUBOV, A. N. and NISMAN, B. Kh., Moscow, Institute of Bioorganic Chemistry imeni M. M. Shemyakin, USSR Academy of Sciences; Leningrad, Institute of Cytology, USSR Academy of Sciences

[Abstract] The neurotoxin M<sub>10</sub> of the Central Asian scorpion (*Buthus eupeus*) venom was chemically modified with 2,4-dinitro-5-fluorophenylazide with the object of synthesizing a biologically active photosensitive derivative

(DNFA-M<sub>10</sub>) whose effect on the sodium channels of electrically excitable membrane could then be investigated through fixation of potential on neuroblastoma cell membranes. It was found that photoactivation is followed by the formation of the covalent toxin-channel complex. Photolysis of the modified toxin thus results in the covalent modification of the fast sodium channels of the electrically excitable membrane. Further, iodination of DNFA-M<sub>10</sub> with iodine-125 does not cause a decrease in biological activity, which points to the possibility of using <sup>125</sup>I-DNFA-M<sub>10</sub> to investigate molecular organization and isolate the scorpion toxin receptors that are components of sodium channels. Figures 4; references 21. [181-1386]

UDC 547.993.02

AMINOACID SEQUENCE OF NEUROTOXIN M<sub>10</sub> FROM THE VENOM OF THE CENTRAL ASIAN SCORPION *Buthus eupeus*

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GRISHIN, Ye. V., SOLDATOVA, L. N., SHAKHPARONOV, M. I. and KAZAKOV, V. K.,  
Moscow, Institute of Bioorganic Chemistry imeni M. M. Shemyakin, USSR  
Academy of Sciences

[Abstract] This is a continuation of an earlier investigation which dealt with the aminoacid sequences of two insectotoxins I<sub>1</sub> and I<sub>2</sub> from the venom of the scorpion *Buthus eupeus*. In this work, the isolation and determination of aminoacid sequence of the neurotoxin M<sub>10</sub> from that venom are considered. The neurotoxin M<sub>10</sub> produces a distinct paralytic effect on the nervous system of mammals. Following its isolation from whole venom by gel-filtration, fractionation, and purification, the neurotoxin was subjected to tryptic and chemotryptic hydrolysis and its full aminoacid sequence was established; it is shown that the neurotoxin M<sub>10</sub> consists of 65 aminoacid residues with 4 intramolecular disulfide bonds, that it completely lacks residues of threonine, methionine, and histidine, and that its aminoacid sequence resembles that of the neurotoxins AII from the venom of *Androctonus australis* Hector and LV from the venom of *Leiurus quinquestratus* quinquestratus. Figures 3; references 18: 8 Russian, 10 Western. [181-1386]

UDC 577.150.3+577.150.4+577.156+541.182.644

ENZYME STABILIZATION: A KEY FACTOR IN PRACTICAL APPLICATION OF BIOCATALYSIS

Moscow USPEKHI KHIMII in Russian No 5, 1980 pp 737-770

MARTINEK, KAREL, and BIREZIN, I. V., Chemistry Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] A review is presented of physicochemical considerations in enhancing the stability of immobilized enzymes, according particular attention to methods that are useful in chemical technology. The two fundamental approaches that may be utilized in preserving enzymatic activity and specificity consist of enhancement of structural rigidity (either via the introduction of additional intramolecular or inter-domain bonding or of multipoint covalent or physical binding to complementary carrier sites to prepare immobilized heterogenous enzyme preparations) or of effective spatial separation of the enzyme from adverse factors. In the latter case pH inactivation may be avoided by immobilizing the enzyme on a buffered carrier or one that allows for local pH shifts on the surface. As an alternative, the effects of organic solvents may be negated by employing biphasic systems for the enzyme reaction ("water--water-immiscible organic solvent"), or by the incorporation of the enzyme in "reverse" micelles of surface-active agents. Figures 10; references 225: 1 Czech, 1 Polish, 33 Russian, 190 Western. [196-12172]

UDC 665.75.32

## VAPOR DIFFUSION COEFFICIENT OF JET FUELS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 4, 1980 pp 29-31

DUBOVKIN, N. F. and SMIRNOVA, L. N.

[Abstract] The vapor diffusion coefficients of jet fuels were determined by a computational method based on the premise that the dependence of the vapor diffusion coefficients of various substances at 0°C and under a pressure of 0.1 MPa can be described by a linear equation. It is shown that the diffusion coefficient varies in inverse proportion to temperature. The presented formulas are based on the processing of experimental data on individual hydrocarbons of various homologous series, alcohols, waters, and certain fuels, and are useful in view of the fact that the experimental determination of vapor diffusion coefficients for individual jet fuels is extremely difficult. Figures 2; references 9: 8 Russian, 1 Western. [162-1386]

UDC 543.87+75.521.3

## EFFECT OF ADDITIVES ON THE PRONENESS OF JET FUELS TO FORM DEPOSITS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 4, 1980 pp 26-29

SEREGIN, Ye. P., GORODETSKIY, V. G. and GOLENEV, N. P.

[Abstract] Modern jet fuels are treated with various additives to prevent oxidation, wear, corrosion, and other undesirable phenomena. In this connection, it was of interest to investigate the effect of these additives on scale formation in jet engines, as characterized by the thermostability index TI (ratio of amount of scale forming on the heat-transfer surface when using the fuel tested as compared to a standard fluid) and by the onset temperature of scaling  $T_{o.s.}$ . Tests based on these criteria showed that the additives used to prevent water crystal-formation produce a detergent effect,

thus somewhat reducing scaling. As for the anti-oxidation additives, when added in small concentrations (0.003%) they do not change the TI, but in large concentrations (0.01-0.2%) they improve the TI somewhat by reducing scaling, without, however, affecting  $T_{0.8}$ . Dispersing additives are more effective than anti-oxidation additives in reducing scaling: the PMAN-2 additive, e.g. increases  $T_{0.8}$  and reduces TI when added in concentrations of as little as 0.05%. As for anti-wear additives, they do not affect TI and  $T_{0.8}$  significantly. Thus, of the additives tested, dispersing additives (PMAN-2, TP and KAP-25) are most promising so far as the reduction of scaling is concerned. Research in that direction should be continued. References: 5 Russian. [162-1386]

UDC 62-631.2:629.113

#### EVALUATION OF THE ANTIKNOCK VALUE OF GASOLINES BY LABORATORY TECHNIQUES UNDER ROAD-TEST CONDITIONS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 4, 1980 pp 24-26

AZEV, V. S., KITSKIY, B. P., MALYKHIN, V. D. and GORYACHYI, Ya. V.

[Abstract] To elucidate the relationship between the results of gasoline road tests and the octane number, the antiknock characteristics of various gasolines (leaded Ekstra and leaded and unleaded AI-93 as well as experimental gasolines containing from 0.34 to 0.82 g (tetraethyl or tetramethyl lead per kg) were investigated by laboratory techniques in road tests on an AZLK-412 automobile, on using two different engines, one with a compression ratio of 8.8 and the other, with 8.1. The findings demonstrate that the principal factor in knocking during car acceleration is the antiknock value of the lighter fractions of gasoline. Given the current limitations on automobile speed and the frequent starting and stopping of automobiles under urban conditions, the mode of acceleration affects the requirements for the antiknock value. By determining the octane number of the low-boiling gasoline fractions by the laboratory method it is possible to predict the antiknock value of these fractions under road conditions. References: 7 Russian. [162-1386]

## OPTIMAL CETANE NUMBER OF DIESEL FUELS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, 1980 pp 19-21

ROSSINSKIY, V. M. and ENGLIN, B. A., All-Union Scientific Research Institute of Petroleum Reprocessing

[Abstract] To assure the easy starting and reliable performance of Diesel engines at low temperatures, many investigators recommended fuels with a wide range of cetane numbers (CN). Results of experiments on the effect of Diesel fuel CN on the performance parameters, on carbon deposition and wear and tear of the motor parts were reported. The most reasonable CN was  $45 \pm 2$ , assuring easy starting, economical and reliable performance of the motor and an acceptable exhaust smoke content. Lowering of the CN from 50-56 to 44-45 decreased fuel consumption by 3-6 percent while maintaining adequate performance dynamics under maximum load. A point was made that, along with a minimal CN, an upper limit for the CN should be established, especially for Diesel fuels used in summer. An all-season fuel appeared to be impractical. References: 8 Russian.  
[150-7813]

## PRODUCTION OF NONETHYLATED GASOLINE AI-93 BY THE COMBINATION OF CATALYTIC REFORMING AND SELECTIVE HYDROCRACKING PRODUCTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, 1980 pp 3-6

MASLYANSKIY, G. N., GEORGIYEVSKIY, V. Yu., ROZENBLIT, A. B., et al

[Abstract] The goal of this study was to develop a method for production of AI-93 gasoline using selective hydrocracking products. Selective hydrocracking (SH) of a reforming catalysis product with an octane number 94.2 yielded gasoline with a 99.2 octane number and a 92.5 percent yield. Hydrogen consumption in this reaction was 0.2 percent. Various mixtures of the reforming and refining materials were subjected to selective hydrocracking. Optimal results were obtained with mixtures of a 70 percent of reforming material and 30 percent of refining material, which yielded a base component with an octane number of 95. The addition of 15 percent of isopentane to this material yielded nonethylated gasoline AI-93. One of the advantages

of the production of a base component is a 20 percent decrease in the consumption of the crude oil. This results from the use of low-octane gasoline refining products. The addition of high octane isoparaffine components may be cut in half. Figures 2; references 9: 6 Russian, 3 Western.  
[150-7813]

## INTERACTION OF ACID CHLORIDES AND BROMIDES OF DIALKYL PHOSPHOROUS ACIDS WITH TETRAHALIDES OF TIN

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 50, No 3, 1980 pp 518-527  
manuscript received 15 Mar 79

MURATOVA, A. A., SOBANOVA, O. B., YARKOVA, E. G., SARYCHEVA, T. I., KHRAMOV, A. S. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] It was demonstrated in a previous study (1976) that the interaction of dimethyl chlorophosphite with tin chloride results in the complex  $[(\text{MeO})_3\text{P}]_2\text{SnCl}_4$ , which differs somewhat in its properties from the complex produced directly from trimethyl phosphite. As a continuation of this research and for the purpose of revealing the general nature of this phenomenon, studies were made of reactions of acid chlorides and bromides of dimethyl, diethyl and dibutyl phosphorous acids with tin chloride and tin bromide. The reactions were carried out with a ratio of initial reactants of 4:1 and 2:1 in an atmosphere of argon in a medium of pentane or without a solvent at approximately  $-10^\circ\text{C}$  with the reaction mixtures then held for 3 to 60 24-h periods at approximately  $0^\circ\text{C}$  or at  $45^\circ\text{C}$  for 10 h. It is demonstrated that complexes with the same composition of  $[(\text{RO})_3\text{P}]_2\text{SnX}_4$  but produced by different methods differ in their properties. It is demonstrated further that complexes with this composition produced by different methods differ neither in terms of their geometric and conformational structure nor in terms of the donor atom of the ligand. On the basis of IR spectroscopy data it is shown that the structure of complexes of trimethyl phosphite with tin chloride produced from a chlorophosphite and phosphite is of an identical nature. Dialkyl halogen phosphites interact with tetrahalides of tin to form alkyl dihalogen phosphites and complexes of trialkyl phosphites with tetrahalides of tin. Differences observed in transformations of complexes with the structure  $[(\text{RO})_3\text{P}]_2\text{SnX}_4$  produced by different methods are caused by the presence in one case of alkyl dihalogen phosphites in the reaction mixture and these differences are apparently related to their specific solvation. For the purpose of establishing the influence of alkyl dihalogen phosphites on the nature of the transformation of  $[(\text{RO})_3\text{P}]_2\text{SnX}_4$  complexes, model reactions were carried out between trialkyl phosphites and tin chloride in the presence of an individual alkyl dichlorophosphite whose quantity was varied from catalytic to quantities exceeding

an equimolar ratio with the phosphite. The results of experiments demonstrated that differences in the properties of complexes obtained by different methods are related to the presence in one case of alkyl dihalogen phosphites in the reaction mixture, whereby these phosphites can evidence both nucleophilic and electrophilic properties. In both cases the solvation by these phosphites of  $[(RO)_3P]_2SnX_4$  complexes must result in considerable inhibition of the isomerization reaction. Specific solvation favors the occurrence of a dealkylation reaction and redox transformation. The isomerization reaction takes place to a lesser extent and is characteristic only of complexes of trimethyl phosphite. Figures 2; references 10: 5 Russian, 5 Western.  
[146-8831]

UDC 541.67+547.241.541.8'284'661.718.2

DIPOLE MOMENTS OF ORGANOPHOSPHORUS COMPOUNDS: XVIII. INVESTIGATION OF THE SPACE STRUCTURE OF DERIVATIVES OF PHOSPHORINANONE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 50, No 3, 1980 pp 527-533  
manuscript received 2 Mar 79

PATSANOVSKIY, I. I., ISHMAEVA, E. A., LOGUNOV, A. P., BOSYAKOV, Yu. G., BUTIN, B. M., SHISHKIN, S. K. and PUDOVIK, A. N., Kazan' State University imeni V. I. Ul'yanov-Lenin and Kazakh SSR Academy of Sciences Institute of Chemical Sciences

[Abstract] The results are given of a study of a number of dimethyl-substituted phosphorinanones (I to X) for which a determination was made of dipole moments (DM's) and Kerr constants (mK's). It had been established by means of IR and PMR spectroscopy that compounds I to X exist in chair form with axial (I to III and VI to X) and equatorial (IV and V) orientation of the P=X bond. Compounds I to V represent trans-geometrical isomers with equatorial methyl groups at ring positions 2 and 5, and compounds IX and X, the corresponding cis-isomers. For phosphorinanones IX and X the assumption had been made that the axial  $CH_3$  group is in position 2. The experimental DM's for compounds I to V equal 3.6, 3.7, 3.83, 3.86 and 4.03 D, respectively. The computed values of dipole moments are close to the experimental. Axial and equatorial isomers have close values of dipole moments. The components of dipole moments in terms of coordinate axes for compounds I to V are given in a table. The experimental dipole moments for compounds VI to X prove to be higher than for I to V. This is related to the addition at position 2 of the ring of an axial methyl group which results in some change in the geometry of the compounds and in the appearance of additional intramolecular electronic interaction. In view of certain features of phosphorinanones,

the dipole moment method proved to be unsuitable for an unambiguous determination of the orientation of exocyclic substituents at the phosphorus. New interesting experimental data were obtained on the polarity of 10 derivatives of phosphorinanone with PIV. The polarity of molecules of these compounds increases regularly when going from derivatives with a phosphoryl to compounds with a thio- and selenophosphoryl group. In the phosphorinanones studied is observed the same pattern in the change in polarity of the P=X bond as in a number of acyclic compounds of phosphorus with P-C bonds. A calculation of Kerr constants,  $mK$ 's, was made for each isomer as a function of the angle of turn of the benzene ring in relation to the P-C<sub>ar</sub> bond. It was demonstrated that  $mK$ 's increase uniformly when going from compounds with a P=O and compounds with a P=S and P=Se bond in keeping with the increase in the polarizability of the P=X bond. It was not possible to make an unambiguous determination of the orientation of exocyclic substituents at phosphorus on the basis of Kerr constants. As far as the degree of rotation of the benzene ring around the P-C<sub>ar</sub> bond is concerned, it can be assumed that there is a great preference for parallel positioning of the benzene ring. Experimental data obtained on  $mK$ 's for compounds III, V, VIII and X represent the first data on the polarizability of organophosphorus compounds containing a selenophosphoryl group. The results are also given of investigations of phosphorinanones I to X by means of NMR  $^{31}P$  spectroscopy. The individuality of each phosphorinanone studied is proven by the fact that the spectra of all these compounds represent a distinctly pronounced unique signal. A table is given of chemical shifts for compounds I to X. NMR  $^{31}P$  spectra were obtained with a KGU-4 NMR  $^{31}P$  instrument at a frequency of 10.2 MHz in relation to 85 percent  $H_3PO_4$ . The employment of all the experimental methods used made it possible to determine the orientation of  $CH_3$  groups in cis-2,5-dimethyl-substituted phosphorinanones. Figures 1; references 24: 16 Russian, 8 Western.

[146-8831]

## SYNTHESIS AND ISOMERIZATION OF 2-(3'-CHLORALKOXY)-1,3,2-OXAZAPHOSPHORINANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 50, No 3, 1980 pp 533-537  
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NURETDINOVA, O. N. and NIKONOVA, L. Z., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov and USSR Academy of Sciences Kazan' Branch

[Abstract] The results are given of a study of the isomerization of certain 2-(3'-chloralkoxy)-1,3,2-oxazaphosphorinanes for the purpose of determining the influence of the size of the ring of the parent amidophosphite and of the nature of substituents in it on the direction of Arbusow rearrangement in a number of 3-chloralkyl ethers. The parent six-member cyclic amidophosphites were produced by reacting the respective acid chlorides with oxyethanes in the presence of anhydrous  $\text{ZnCl}_2$  or with 1-chlorobutane-3-ol in the presence of a base. A study is made of the isomerization of cyclic amidophosphites containing primarily isomers with a chloralkoxyl group structure of  $>\text{POCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl}$ . Unlike certain five-member amidophosphites, the intramolecular rearrangement of which can take place along a single direction with the formation of only a single phosphonate, as the result of the isomerization of 2-(3'-chloralkoxy)-1,3,2-oxazaphosphorinanes a mixture of phosphonates with a chloralkoxyl group structure of  $>\text{POCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl}$  and  $>\text{POCH}_2\text{CH}_2\text{CHClCH}_3$  is practically always produced. The ratio of the two phosphonates formed depends both on the nature of substituents in ring (R and  $\text{R}^1$ ) and on the structure of the alkoxyl radical ( $\text{R}^2$ ). The ratio of the two types of phosphonates produced in isomerization was determined from NMR  $^{31}\text{P}$  spectra. Tables of constants are presented for mixtures of phosphonates produced as the result of the isomerization of seven 2-(3'-chloralkoxy)-1,3,2-oxazaphosphorinanes. NMR  $^{31}\text{P}$  spectra were recorded with a KGU-4 NMR spectrometer at a frequency of 10.2 MHz. Reference: 1 Russian.  
[146-8831]

PRODUCT OF 1,3 RING ATTACHMENT OF *n*-NITROBENZALDEHYDE TO ISOCYANATE DIETHYL PHOSPHITE AND ITS HYDROLYSIS IN SOLUTION

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[Abstract] An earlier study demonstrated that isocyanate dialkyl phosphites in reactions with aromatic aldehydes form products of 1,3 ring attachment. As a continuation of research along this line, the results are given of a study of the interaction of isocyanate diethyl phosphite with *n*-nitrobenzaldehyde, which resulted in the separation of a ring adduct, i.e., 2-*n*-nitrophenyl-3,3-diethoxy-5-oxo-1,4,3-oxazaphosphol-3-ene (I). When the reaction was carried out in ether, in which compound I dissolves rather poorly, its yield reached 18 percent because of its rapid separation from the solution. When the isocyanate diethyl phosphite was reacted with benzaldehyde and the methylene chloride solvent was replaced by hexane, the yield of the final product was increased from eight to 40 percent. In the crystalline state the oxazaphospholenes studied are not hydrolyzed when stored for two years and longer. When the isocyanate diphenyl phosphinite was reacted with *n*-nitrobenzaldehyde the corresponding oxazaphospholene was not able to be produced. Only the product of its hydrolysis was separated from the reaction mixture, i.e.,  $\alpha$ -diphenyl phosphine oxido- $\alpha$ -*n*-nitrophenyl methyl carbamate. Compound I in solution is rapidly hydrolyzed and the formation of  $\alpha$ -diethoxyphosphone- $\alpha$ -*n*-nitrophenyl methyl carbamate occurs. The  $\alpha$ -diphenyl phosphine oxido- $\alpha$ -*n*-nitrophenyl methyl carbamate formed in the reaction of isocyanate diphenyl phosphinite with *n*-nitrobenzaldehyde is the product of the hydrolysis of the ring adduct NMR  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  spectra were recorded with a WP-80 spectrometer. Chemical shifts of carbon protons and nuclei were indicated in relation to  $(\text{CH}_3)_4\text{Si}$  and chemical shifts of phosphorus nuclei in relation to 85 percent  $\text{H}_3\text{PO}_4$ . IR spectra were recorded with a UR-20 spectrometer in the 500 to 3600  $\text{cm}^{-1}$  range. PMR and NMR  $^{13}\text{C}$  spectra are shown for  $\alpha$ -diethoxy phosphone  $\alpha$ -*n*-nitrophenyl methyl carbamate. Figures 1; references: 5 Russian.  
[146-8831]

## RETRO-ARBUSOW REARRANGEMENT OF ETHERS OF ACIDS OF ARSENIC

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GAMAYUROVA, V. S., SAVDUR, V. I. and CHERNOKAL'SKIY, B. D., Kazan' Chemical Technological Institute imeni S. M. Kirov

[Abstract] Although numerous unsuccessful attempts have been made to carry out Arbusow rearrangements with compounds of arsenic, it has been demonstrated that ethers of alkyl arsonic acids and oxides and sulfides of ternary arsines under the effect of halogen alkyls are transformed into the corresponding ethers of acids of trivalent arsenic. A similar transformation occurs under a thermal influence on ethers of alkyl arsonic and dialkyl arsinic acids and on oxides of trialkyl arsines. These reactions are here called retro-Arbusow rearrangement. It is demonstrated that the interaction of ethers of diphenyl and dialkyl arsinic and phenyl arsonic acids with halogen alkyls takes place along three major lines: retro-Arbusow rearrangement, an exchange reaction and a redox reaction. Thermal retro-Arbusow rearrangement apparently takes place under nucleophilic substitution conditions according to either a mono- or bimolecular mechanism. Molecules of the original substance apparently act as the nucleophilic substrate and electrophilic reagent. The addition of electrophilic reagents to ethers of alkyl arsonic acids considerably lowers the temperature for the beginning of interaction (TNV). The TNV of ethers of alkyl arsonic acids when reacted with halogen alkyls depends substantially on the nature of the halogen alkyl. How this rule operates for ethers of arsinic acids is investigated here. Determinations were made of the TNV of the propyl ether of diphenyl arsinic acid when reacted with a number of halogen-substituted propyls. The results demonstrate that the TNV depends heavily on the generalized electrophilic activity of the halogen alkyl, whereby the least lowering of the TNV is produced by propyl chloride, and the most by propyl iodide. A study of the products of the interaction of ethers of diphenyl arsinic and phenyl arsonic acids with benzyl bromide demonstrated that the main products are ethers of diphenyl arsinic and phenyl arsonic acids, where the hydrocarbon radical of the alkoxy group corresponds to the halogen alkyl used in the reaction. Here the exchange reaction is the predominant one. The yield of exchange products equaled 75 to 92 percent; in addition, products of a redox reaction are separated, i.e., the individual ethers of diphenyl arsinous and phenyl arsonous acids, as well as benzaldehyde. An investigation of the products of the reaction of ethers of dialkyl arsinous acids with benzyl bromide demonstrated that the dominant direction of this reaction is retro-Arbusow rearrangement. The conductometric method was employed for the purpose of identifying possible intermediate products, such as salts of alkoxy arsonium, in reactions between ethers of arsinic and arsonic acids with halogen alkyls. The results of a conductometric investigation

confirmed the hypothesis regarding the formation in the reaction of alkoxy arsonium salts as intermediate products. A diagram is suggested to illustrate the interaction of ethers or arsinic and arsonic acids with halogen alkyls, on the basis of the data obtained. First takes place a nucleophilic attack of the arsenyl group of the ether on the electrophilic reagent, as the result of which an alkoxy arsonium salt forms. Further transformation of the alkoxy arsonium salt is determined by the conditions for carrying out the reaction and by the nature of the reacting components. An exchange reaction is most typical of ethers of diaryl arsinic and aryl arsonic acids. A rise in temperature of the reaction results in the preferential occurrence of redox reactions for aromatic derivatives. Retro-Arbusow rearrangement is most typical of ethers of dialkyl arsinic and alkyl arsonic acids. It is concluded that retro-Arbusow rearrangement is characteristic of derivatives of four-coordination arsenic having at least one arsenic-aliphatic carbon atom bond. Retro-Arbusow rearrangement is of a universal nature for aliphatic derivatives of four-coordination arsenic, since it takes place for oxides and sulfides of ternary arsines and for ethers of arsinic and arsonic acids. Aromatic derivatives of four-coordination arsenic undergo other transformations under the influence of halogen alkyls. Figures 1; references 14: 13 Russian, 1 Western. [146-8831]

UDC 546.185

#### AMMONOLYSIS OF TRIAMIDOHALOGEN PHOSPHONIUM HALIDES

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MARCHENKO, A. P., KOYDAN, G. N. and KURDYAVTSEV, A. A., Ukrainian SSR Academy of Sciences Institute of Organic Chemistry

[Abstract] It has been found that in the ammonolysis of hexaalkyl triamido-halogen phosphonium halides are formed halogen hydride salts of hexaalkyl triamidophosphazohydrides, which under the influence of an aqueous alkali solution are transformed into triamidophosphazohydrides. Triamidophosphazohydrides are little-studied compounds which are of considerable interest as starting substances for the synthesis of various new types of phosphazo compounds, such as triamidophosphazoalkanes, -arenes, -silanes, etc. The structure of hexaalkyltriamidophosphazohydrides and their halogen hydride salts has been confirmed by the data of elemental analysis and IR and NMR  $^{31}\text{P}$  spectroscopy. To produce halogen hydride salts of triamidophosphazohydrides, in a solution, cooled to  $0^\circ\text{C}$ , of 0.01 mole of triamidohalogen

phosphonium halide in 50 ml of dichloroethane or benzene is admitted by increasing weight 0.02 mole of anhydrous ammonia for 10 to 15 min. The precipitated ammonium halide is separated, the filtrate is concentrated by evaporation and the residue is crystallized. Data are given on tris(N,N-diethylamido)amidophosphonium iodide, tris(N,N-diethylamido)-amidophosphonium bromide and tris(N,N-dihexylamido)amidophosphonium chloride. Triamidophosphazohydrides are produced by vigorously stirring 0.01 mole of a halogen hydride salt of a triamidophosphazohydride for 5 to 10 min with 20 ml of a 40 percent aqueous alkali solution. The organic salt is extracted with 2 X 20 ml of benzene. The benzene solution is dried over sodium sulfate and is filtered, the filtrate is concentrated by evaporation and the residue is vacuum distilled. The properties are given, of the substances produced: tris(N,N-diethylamido)phosphazohydride, tris(N,N-dihexylamido)phosphazohydride and tris(N,N-diethylamido)iodophosphonium iodide. References 3: 2 Russian, 1 Western.

[146-8831]

UDC 547.241+547.26'118

#### O-PHOSPHORYLATION OF KETOPHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHEMII in Russian Vol 50, No 3, 1980 pp 682-683  
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[Abstract] Previously unknown  $\alpha$ -dialkoxyphosphonyl vinyl phosphites (II) have been formed as O-derivatives in the phosphorylation of acyl phosphonates (I) by monochlorophosphites in the presence of triethylamine. The structure of compounds II has been determined from the data of IR and NMR  $^1\text{H}$  and  $^{31}\text{P}$  spectroscopy and of chemical transformations. They oxidize relatively easily and attach sulfur and undergo an Arbusov rearrangement with the formation of substituted vinyl phosphates (III to V). In the IR spectra of compounds II to V there is an absorption band at  $1630\text{ cm}^{-1}$ , and in the divinyl phosphate (V) there is doublet absorption in this region. Diethyl chlorophosphite is produced with a yield of 71 percent from  $\text{PCl}_3$  and alcohol in the presence of pyridine (a medium of ether at  $20^\circ\text{C}$  for 24 h). Data are presented on O,O-diethyl-O-(1-diethylphosphinyl vinyl) phosphite, O,O-diethyl-O-(1-diethylphosphinyl vinyl) thiophosphate, O-ethyl-O-(1-diethylphosphinyl vinyl)- $\alpha$ -ethoxycarbonyl methyl phosphonate and O-ethyl-O-(2,2-dichlorovinyl)-O-(1-diethylphosphinyl vinyl) phosphate. References:

3 Russian.

[146-8831]

## REARRANGEMENT OF OXAZAPHOSPHOLINES INTO DIAZOPHOSPHOLANONES

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manuscript received 13 Aug 79

GOLOLOBOV, Yu. G. and NESTEROVA, L. I., Ukrainian SSR Academy of Sciences  
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[Abstract] It had been established earlier (1977) that 1,3,2-oxazaphosphol-4-ines with trivalent phosphorus containing an alkoxy group in the 5 position can be thermally rearranged into diazadiphosphanes. It is demonstrated here that the addition of a monosubstituted amino group to the phosphorus of phospholines results in the fact that ring opening is accompanied not by dimerization to diphosphanes, but by the transfer of a proton from the nitrogen to the carbon. The final product of the reaction is not the expected phosphazene, but its cyclic isomer. The structure of this isomer has been proven by means of physical chemical methods and by intentional synthesis. The transformation of the intermediately formed phosphazenes into diazaphospholanones represents the distinctive intramolecular amidation of complex ethers on account of opening of the P=N bond of phosphazenes, a reaction previously unknown for a compound of 2-coordination phosphorus. To produce 1,3-di-tert-butyl-2-phenoxy-1,3,2-diazaphospholan-4-one, an equimolar (0.1 mole each) mixture of 3-tert-butyl-2-chloro-5-phenoxy-1,3,2-oxazaphosphol-4-ine and trimethyl silyl-tert-butylamine in 300 ml of ether is held for two 24-h periods and the solvent and trimethyl chlorosilane are distilled off. In the residue is a solid substance. After crystallization from ether at -78°C and sublimation, the boiling point is 80°C with a yield of 60 percent. The cyclic isomer referred to above, i.e., the diazaphospholanone, is produced as follows: A benzene solution of phenyl dichlorophosphite, tert-butyl-anide of tert-butylaminoacetic acid (0.1 mole each) and an excess of triethylamine are boiled for 12 h, filtered, concentrated by evaporation and cleaned. The diazaphospholanone has a boiling point of 80°C and is produced with a yield of 80 percent. The data of IR, PMR, NMR <sup>31</sup>P and mass spectroscopy are given. References: 2 Russian. [146-8811]

## PHOSPHORYLATION OF DIMETHYL ETHINYL CARBINOL WITH PHOSPHORUS PENTACHLORIDE

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NOZINOV, V. G., KOLBINA, V. Ye. and GLUKHIKH, V. I., Irkutsk State University imeni A. A. Zhdanov and Irkutsk State University Institute of Petrochemical and Carbon Chemical Synthesis

[Abstract] It has been demonstrated that the interaction of phosphorus pentachloride with dimethyl ethinyl carbinol in a solution or in a heterogeneous medium results in the formation of C-phosphorylated products. By treatment with  $\text{SO}_2$ , the crystalline complex separated is converted into the dichloroanhydride of phosphonic acid. It has been demonstrated from the data of NMR spectroscopy that the products of the phosphorylation of dimethyl ethinyl carbinol are similar to the compounds produced in the phosphorylation of isopropenyl acetylene. In the NMR  $^{31}\text{P}$  spectrum of a solution of the complex in nitrobenzene are present two signals close in intensity, belonging to a 2-methyl-3,4-dichloro-2-butene-1-trichlorophosphonium cation and a 3-methyl-2,4-dichloro-2-butene-1-trichlorophosphonium cation. The NMR  $^{31}\text{P}$  spectrum of a freshly prepared dichloroanhydride of phosphonic acid contains two identical very close signals belonging to dichloroanhydrides of 2-methyl-3,4-dichloro-2-butene-1-phosphonic acid and 3-methyl-2,4-dichloro-2-butene-1-phosphonic acid. In the spectrum of a distilled mixture of these two latter compounds has been detected a signal belonging to the dichloroanhydride of 2-methyl-3-chloro-1,3-butadiene-1-phosphonic acid. A chemical shift is related to the dichloroanhydride of 3-methyl-2-chloro-1,3-butadiene-1-phosphonic acid. A diagram is suggested for the phosphorylation of dimethyl ethinyl carbinol. To a dispersion of 144.3 g of phosphorus pentachloride in 250 ml of absolute benzene at 10 to 15°C are added dropwise while stirring 14.5 g of dimethyl ethinyl carbinol in 10 ml of benzene. After a few days the precipitate of the complex is filtered off and is treated with  $\text{SO}_2$ . After evaporation of the volatile products under a vacuum is produced a mixture of dichloroanhydrides of 2-methyl-3,4-dichloro-2-butene-1-phosphonic acid and 3-methyl-2,4-dichloro-2-butene-1-phosphonic acid. References: 3 Russian. [146-8831]

## SYNTHESIS OF DIALKYL PHOSPHONE-5-HEXANONES

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BREL', A. K., RAKHIMOV, A. I., FILDIMONOVA, L. M. and BURYAKOVA, T. A., Volgograd Polytechnical Institute

[Abstract] A new method is suggested for producing dialkyl phosphone-5-hexanones by the reaction of the homolytic attachment of dialkyl phosphites to alkyl acetone. The yield of dialkyl phosphone-5-hexanones is 60 to 65 percent and the reaction takes place chiefly through the double carbon-carbon bond without touching the carbonyl group. The optimal parameters have been found for carrying out the attachment reaction, such as the ratio of reactants, the amount of initiator and temperature conditions. A high-boiling high-temperature initiator, e.g., 4-methyl-4-tert-butyl-peroxy-2-pentanone, is used. The structure of the compounds produced has been confirmed by the data of an elemental analysis and by determination of molecular weight and refraction and by IR and PMR spectroscopy. Dimethyl phosphone-5-hexanone is produced with a yield of 67 percent, with a boiling point of 129 to 132°C under 2 mm Hg. Diethyl phosphone-5-hexanone is produced with a yield of 63 percent, with a boiling point of 139 to 141°C under 1 to 1.5 mm Hg. The purity of the substances obtained was determined by means of thin-layer chromatography, using "Silufol" plates and an ether : alcohol system. Reference: 1 Western.  
[146-8831]

## INTERACTION OF 2-ALKOXYTETRAHYDROPYRANES WITH PHOSPHORUS TRICHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 50, No 3, 1980 p 687 manuscript received 9 Jul 79

GAZIZOV, M. B., RAZUMOV, A. I., GIZATULLINA, I. Kh. and OSTANINA, L. P., Kazan' Chemical Technological Institute imeni S. M. Kirov

[Abstract] It has been discovered for the first time that 2-alkoxytetrahydropyrans (I) react at room temperature with phosphorus trichloride (II). There have hitherto been no published data on the interaction of cyclic acetals and 2-alkoxytetrahydropyrans with chlorides of 3-coordination phosphorus. When phosphorus-containing substituents are added to 2-alkoxytetrahydropyrans, bis-phosphoric compounds are formed with various types of

coordination of the phosphorus atoms. The 2-chlorotetrahydropyran produced as a reaction product is easy to produce in individual form. It has a boiling point of 46°C under 15 mm Hg. Some of the products formed are poorly stable and decompose in attempts at vacuum distillation. Identified as products are  $\text{OCH}_2\text{P}(\text{O})(\text{OCH}_3)_2$  and  $\text{OCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ . The structure and composition of these last two compounds have been proved by the method of PMR spectroscopy and by elemental analysis for phosphorus, carbon and hydrogen.

[146-8831]

UDC 547.241

#### INTERACTION OF METHYLENEDIPHOSPHORUS<sup>III</sup>-CONTAINING COMPOUNDS WITH HYDROGEN CHLORIDE

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PRISHCHENKO, A. A., NOVIKOVA, Z. S. and LUTSENKO, I. P., Moscow State University imeni M. V. Lomonosov

[Text] Studies have been made of the interaction of a number of methylene-diphosphorus<sup>III</sup>-containing compounds including alkyl and phenyl substituents and chlorine atoms at the phosphorus atoms, with hydrogen chloride. It has been determined that the direction of the reaction is governed primarily by the electrophilic and nucleophilic properties of atoms of 3-coordination phosphorus in a number of these compounds and also depends on the volume of substituents at phosphorus atoms. Tetrachloromethylene diphosphine, having the lowest nucleophilicity, does not react with dry HCl, whereas tetraalkylmethylene diphosphines, representing compounds with the highest nucleophilicity of phosphorus atoms, easily attach two molecules of HCl to form crystalline diphosphonium salts. Dichloroanhydrides of methylene dialkyl(aryl)phosphinous acids, which come in the middle in terms of the electrophilicity and nucleophilicity of phosphorus atoms, react with HCl with splitting of the phosphorus-carbon bond. Splitting of the phosphorus-carbon bond in the originally formed phosphonium salt takes place as the result of a nucleophilic attack of the chlorine anion on the atom of 3-coordination phosphorus and of the subsequent irreversible transformation of the ylide into phosphine. The reaction takes place easily for compounds with substituents of low volume (such as Me and Ph) at the phosphorus atoms, at a temperature of 20 to 60°C, and with somewhat greater difficulty for compounds containing substituents with an iso-structure, such as *i*-Bu, *i*-Pr and cyclo-C<sub>6</sub>H<sub>11</sub>, whereby the reaction takes place at 80 to 120°C. The

reaction practically does not take place for compounds with tert-butyl substituents in the molecule. Data are given on the compounds produced, including the dichloride of methylene bis-(dimethyl phosphonium), the dichloride of methylene bis-(diisopropyl phosphonium) and a mixture of compounds. The composition and structure of the compounds produced have been confirmed by the data of elemental analysis and NMR  $^1\text{H}$  and  $^{31}\text{P}$  spectroscopy. References: 2 Russian.  
[146-8831]

UDC 547.241

#### STABILITY OF DIPHOSPHACYCLOPROPANES

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PRISHCHENKO, A. A., NOVIKOVA, Z. S. and LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] The results are given of an investigation of the interaction of diacid halides of methylene dialkyl phosphinous acids (I) with alkaline metals such as potassium and sodium and a melt of them, whereby it was demonstrated that the ring formation of compounds I takes place under mild conditions of 0 to +10°C when employing a liquid alloy of potassium and sodium in a medium of hydrocarbons. On the other hand, both metallic potassium and sodium react with compounds I only in the molten state under severe conditions of 70 to 100°C. In both cases 1,2,4,5-tetra(alkylphospha)cyclohexanes were produced with high yields. Under mild conditions for carrying out ring formation, it was possible to record in the reaction mixture by the method of NMR  $^{31}\text{P}$  spectroscopy the formation of di(tert-butylphospha)cyclopropane, whose content in a mixture with tetra(tert-butylphospha)cyclohexane equaled 80 percent. It was not possible under similar conditions to record di(isopropylphospha)cyclopropane. Apparently, the reduction of space impediments at phosphorus atoms in diphosphacyclopropanes considerably hastens their dimerization. Di(tert-butylphospha)-cyclopropane dimerizes slowly and irreversibly at 20°C in pentane to form tetra(tert-butylphospha)cyclohexane in the form of colorless acicular crystals. The composition and structure of the tetraphosphacyclohexanes have been confirmed by elemental analysis and NMR  $^1\text{H}$  and  $^{31}\text{P}$  spectroscopy. Spectroscopic data testify to the fact that in the tetraphosphacyclohexanes produced by the new method identical substituents at phosphorus atoms are found in the trans position. Data are given on 1,2,4,5-tetra(isopropylphospha)cyclohexane, with a yield of 90 percent and a boiling point of 115°C under 0.01 mm Hg, and on 1,2,4,5-tetra(tert-butylphospha)cyclohexane with a yield of 95 percent and a boiling

point of 141 to 142°C. The results obtained agree with a recently published study by Baudler and Saykowski (1978) in which some of these compounds were produced by another method but with low yields. References 2: 1 Russian, 1 Western.  
[146-8831]

UDC 542.91:547.1'118

#### SYNTHESES OF CHLOROMETHYLPHOSPHINE OXIDES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 3, 1980 pp 669-672 manuscript received 29 Jan 79

TSEVTKOV, Ye. N., KRON, T. Ye., and KABACHNIK, M. I., The Institute of Element-Organic Compounds, USSR Academy of Sciences, Moscow

[Abstract] A procedure for direct conversion of acetoxymethylphosphine oxide into chloromethylphosphine oxides using gaseous HCl in an AcOH distillation is described. Procedures with oxides of tri(chloromethyl)phosphine, methyldi(chloromethyl)phosphine, and dimethylchloromethylphosphine involved 3 variants each, the process involving substitution of chlorine in place of the acetoxy group. Gaseous HCl catalyzed the reactions. Formulas, references 17: 10 Russian, 7 Western.  
[143-12111]

UDC 541.6:547.1'118

#### THE CRYSTALLINE AND MOLECULAR STRUCTURE OF BIS(METHYL-o-CARBONYL)CHLOROPHOSPHINATE

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 845-848 manuscript received 16 Mar 79

FURMANOVA, N. G., STRUCHKOV, Yu. T., DECTYAREV, A. N., BREGADZE, V. I., GODOVIKOV, N. N., and KABACHNIK, M. I., Institute of Element Organic Compounds of the USSR Academy of Sciences, Moscow

[Abstract] X-ray diffraction analysis of bis(methyl-o-carbonyl)chlorophosphate, produced by interaction of O-ethyl-bis(methyl-o-carbonyl)phosphate and chlorine, was carried out to determine the degree of distortion of coordination of the phosphorus atom in the presence of voluminous o-carbonyl

substitutes. Binding of the  $\text{CH}_3$  groups in the o-carbonyl nucleus with the oxygen atom of the  $\text{P}=\text{O}$  group is shown. This conformation is not determined by intramolecular steric factors and by interactions with participation of  $\text{CH}_3$  groups since the Van der Waals contact has only a single hydrogen atom of the  $\text{CH}_3$  group with  $\text{B}^{14}$  and  $\text{H}^{14}$  atoms. All the remaining distances for  $\text{CH}_3$  groups significantly exceed the sum of bp. The binding of the  $\text{CH}_3$  groups with the oxygen atom is possibly caused by the nature of molecular packing in the crystal or by electrostatic interaction. Figures 1; references 12: 10 Russian, 2 Western.  
[185-6521]

UDC 541.427:542.955:547.313:546.185'131

#### THE REACTIVITY OF ALKENE ADDUCTS WITH PHOSPHORUS PENTACHLORIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 897-904 manuscript received 9 Feb 79

KROLEVETS, A. A., KOLOMIYETS, A. P., FOKIN, A. V., and PETROVSKIY, P. V.

[Abstract] The effect of solvation on the direction of the reaction of adducts with alkenes,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ , acetic and trifluoroacetic acids and their anhydrides was studied. Nucleophilic reagents cause either dephosphorolation of adducts with release of  $\text{PCl}_3$  or result in vinyl substitution or addition products by the  $\text{C}=\text{C}$  alkene bond as a function of the solvent, temperature and structure of the alkene. Dephosphorolation of adducts exposed to nucleophilic agents is inhibited by nonpolar solvents with weak electrophilic properties or at reduced temperatures. The additional experimental data agree with the epiphosphoric structure of the adducts. References: 10 Russian.  
[185-6521]

## INTERACTION OF DIMETHYLPHOSPHITE AND MONOMETHYLPHENYLPHOSPHONITE WITH 2-METHYL-3,4,5-TRIPHENYLCYCLOPENTADIENE

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 904-909 manuscript received 13 Feb 79

ARBUZOV, B. A., FUZHENKOVA, A. V., GALYAUDINOV, N. I., Chemical Institute imeni A. M. Butlerov and Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] The reactions of dimethylphosphite and monomethylphenylphosphonite with tricyclon--2-methyl-3,4,5-triphenylcyclopentadiene--were studied with respect to the interaction of cyclons with hydrophosphoryl compounds. The reaction proceeds in the absence of catalysts with formation of disconnected  $\beta$ -phosphoneketones which are subjected to prototropic isomerization to connected  $\beta$ -phosphoneketones under the conditions of the reaction. Dimethylphosphorite and monomethylphenylphosphonite do not form products of 1,4-addition to the connected to  $C = C - C = O$  cyclon system with tricyclon, as do alcohols. References 11: 5 Russian, 6 Western.  
[185-6521]

## REACTION OF TRIALKYLPHOSPHITES WITH 1,1,1-TRIFLUOROACETONE

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 910-914 manuscript received 8 Dec 78

KIBARDIN, A. M., GAZIZOV, T. Kh., YEFREMOV, Yu. Ya., ZININ, V. N., MUSIN, R. Z. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov of the Kazan' Branch of the USSR Academy of Sciences

[Abstract] The interaction of trialkylphosphites and 1,1,1-trifluoroacetone was studied by the method of nuclear magnetic resonance of phosphorus to obtain more detailed information on the mechanism of reactions of activated carbonyl compounds with trialkylphosphites. The reaction of trialkylphosphites and 1,1,1-trifluoroacetone forms 2,2,2-trialkoxy-3,5-dimethyl-3,5-bis(trifluoromethyl)-1,4,2-dioxaphospholanes that are slowly isomerized to trialkoxy- $\alpha$ -trifluoromethyl- $\alpha$ -(1-methyl-2,2-difluorovinyl)ethoxyfluorophosphoranes. Figures 2; references 13: 6 Russian, 7 Western.  
[185-6521]

## REACTIONS OF KETOLS WITH ORGANOPHOSPHORUS COMPOUNDS. 9. FORMATION OF 2-SUBSTITUTED OXAPHOSPHOLANES-3 FROM AMIDOPHOSPHITES AND DIACETONE ALCOHOL

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 915-918 manuscript received 27 Feb 79

MUKHAMETOV, F. S., YELISEYENKOV, R. M., RIZPOLOZHENSKIY, N. I., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov of the Kazan' Branch of the USSR Academy of Sciences

[Abstract] Alcoholysis of amidophosphites by  $\beta$ -ketals was studied under different conditions. The two amide groups were substituted with regard to the fact that the anticipated bis( $\gamma$ -ketoalkyl)phosphites were proposed as intermediate products in synthesis of 2-substituted oxaphospholanes-3 from dichloral anhydrides of phosphoric acids and diacetone alcohol. The final products from the reactions in the presence of acetic acid are 2-substituted oxaphospholanes-3. References 11: 10 Russian, 1 Western. [185-6521]

## SYNTHESIS AND ISOMERIZATION OF 2-(3'-CHLOROALKOXY)-1,3,2-AZATHIA-, 1,3,2-OXATHIA- AND 1,3,2-DITHIAPHOSPHOLANES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 918-923 manuscript received 10 Jan 79

NIKONOVA, L. Z., NURETDINOVA, O. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov of the Kazan' Branch of the USSR Academy of Sciences

[Abstract] The series 2-(3'-chloroalkoxy)-1,3,2-azathia-, 2-(3'-chloroalkoxy)-1,3,2-diaza-, 2-(3'-chloroalkoxy)-1,3,2-oxathia- and 2-(3'-chloroalkoxy)-1,3,2-dithiaphospholanes was synthesized and their isomerization was studied. Substitution of the oxygen atoms in position 1 and 3 of the dioxaphospholane cycle by sulphur or nitrogen atoms leads to rearrangement of 2-(3'-chloroalkoxy)-1,3,2-azathia- and diazaphospholanes without disclosure of the cycles regardless of the structure of the chloroalkoxyl group. The direction of the isomerization reaction of 3-chloroalkyl esters of 1,3,2-oxithiaphospholanes depends on the structure of the chloroalkoxyl group. References: 2 Russian. [185-6521]

## THE REACTIVITY OF CYCLIC DERIVATIVES OF PHOSPHORIC ACIDS IN REACTION WITH DIPHENYLDIASOMETHANE

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 934-935 manuscript received 14 Apr 79

OVCHINIKOV, V. V., CHERKASOV, R. A., and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] The reactivity of cyclic and acyclic organophosphorus compounds where the reaction center is one of the atoms in the lateral chain rather than the phosphorus atom, was studied kinetically and thermochemically and the thermal effects of these reactions were studied. The rates and heats of reactions of some derivatives of phosphoric acids with diphenyldiasomethane in p-xylene were measured. The high reactivity and exothermicity of the reactions of cyclic derivatives is shown. These factors are related to the high acceptor capability of cyclic dioxyalkylene substitutes of the phosphorus atom compared to alkoxy groups. References 7: 3 Russian, 4 Western.

[185-6521]

## INTERACTION OF PHOSPHORUS-CONTAINING ESTERS OF PHENYL- AND DIPHENYLBORIC ACIDS WITH AMINES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 952-954 manuscript received 1 Oct 79

ARBUZOV, B. A., YERASTOV, O. A., and NIKONOV, G. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov of the Kazan Branch of the USSR Academy of Sciences

[Abstract] Aminolysis of diphenylboryloxymethylloxymethylphenylphosphines, 2,5-diphenyl-2-boron-1,3,5-dioxaphosphorinane and di(oxymethyl)phenylphosphine was carried out in the presence and absence of paraform. Aminolysis of phosphorus-containing esters of phenyl- and diphenylboric acids by primary and secondary amines proceeds under mild conditions with formation of di-(R-aminomethyl)phenylphosphines in the absence of paraform and of 5-phenyl-1,3-di-R-1,3,5-diazaphosphorinanes in the presence of paraform. There is a correlation between the ease of aminolysis of esters of phenyl- and diphenylboric acids and the capability of alcohols from which the esters were produced to alkylate the amines. References 11: 9 Russian, 2 Western. [185-6521]

## SYNTHESIS AND THE STRUCTURE OF PHOSPHORUS-CONTAINING ESTERS OF PHENYL- AND DIPHENYLBORIC ACIDS

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHIMICHESKAYA in Russian No 4, pp 954-957 manuscript received 1 Oct 79

ARBUZOV, V. A., YERASTOV, O. A. and NIKONOV, G. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov of the Kazan Branch of the USSR Academy of Sciences

[Abstract] Esters of phenyl- and diphenylboric acids and of di(oxymethyl)-phenylphosphine and its oxide and sulfide were produced. The esters of diphenylboric acid were found to exist in open form. The ester with di(oxymethyl)pphenylphosphine, which was found in cyclic form stabilized by intramolecular interaction of the phosphorus- and boron-containing fragments, was an exception. The existence of these compounds in open form means that the energy advantage upon transition of the boron atom to the tetrahedral valent state and transition of hydrogen to the thiophosphoryl and of sodium to the phosphoral groups is inadequate for stabilization of the cyclic form. The stability of the cyclic form apparently affects the course of those reactions in which formation of it is possible. These reactions include the interaction of diols with esters of diphenylboric acid. References.

[185-6521]

UDC 543.70

## ANALYSIS AND PURIFICATION OF ALKYLPHOSPHORIC ACIDS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 25, No 5, 1980 pp 1008-1011 manuscript received 8 Feb 79

RUBLEV, V. V., Moscow Automotive Institute

[Abstract] The various methods of analysis and purification of alkylphosphoric acids during the past 10 years are reviewed. The potentiometric method of determining alkylphosphoric acids in different solvents is based on titration of APA solutions by a standard alcohol solution of KOH and permits determination of APA both individually and in mixtures. Gas-liquid chromatography after methylation is used to identify and quantitatively determine mono- and dialkylphosphoric acids or their salts. The titrimetric method of determining D2EGPA is based on titration of a lauryl benzyldimethylanmonium chloride solution in a two-phase  $H_2O-CHCl_3$  system in an alkaline medium in the presence of thymolphthaleine as an indicator. The

method of differential titration of mono- and dialkylphosphoric acids and also of phosphoric acid by an NaOH solution is used. The basis of APA synthesis is the reaction between the phosphoric anhydride and the corresponding alcohol. Unpurified D2EGPA is initially treated with concentrated hydrochloric acid, then with water and finally with an NaOH solution. Another method of purification recommends that the solution be sequentially flushed with HCl, water and NaOH solution, HCl and water. The different methods of purification permit a purified product with yield of not more than 50 percent to be produced. References 42: 21 Russian, 21 Western. [189-6521]

## PETROLEUM PROCESSING TECHNOLOGY

UPC 665.765--404.038.1.022.39

### ALKYLPHENOXYALKYLSTANNANES AS BIOCIDAL ADDITIVES FOR LUBRICANTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 4, 1980 pp 43-46

BELOV, P. S., TSVETKOV, O. N., KOMAROVA, N. N., KORENEV, K. D., GULO, R. A. and PODDUBNYY, V. N., MINKhIGP [Moscow Institute of Petrochemical and Gas Industry imeni I. M. Gubkin]

[Abstract] Biological damage to oils and lubricants in tropical and subtropical climates, owing to the effect of bacteria and fungi which thrive on hydrocarbons, is a growing problem. In this connection, the antiseptic properties of alkylphenoxyalkylstannanes and particularly of substances having the general formulas  $RC_6H_4OSnR_3$  and  $(RC_6H_4O)_2SnR_2$  was investigated. The inhibiting effect of the synthesized substances on the growth of microorganisms in lubricants was tested. It was established that the structure of the alkylphenol fragment is not an important factor in inhibiting biogenesis. Apparently the interaction of alkylphenoxytriethylstannanes and the vitally important centers of microorganisms is preceded by hydrolysis with the formation of  $-Sn-(C_2H_5)_3$ . Of the substances tested, AFOTAS was found to be the most suitable. It offers complete protection against biological damage to oils MS-20 and AUP and lubricants LS-1, 1-LZ, AEROL, and BAM-3, when added in concentrations of 0.3 wt.%, at temperatures of up to 165°C, for at least 2 years, and it is satisfactorily soluble in lubricants. Thus, AFOTAS can be recommended as an antiseptic for lubricants used to protect petroleum equipment against corrosion in tropical and subtropical climate. References 11: 9 Russian, 2 Western.

[162-1386]

## INTERACTION OF SULFUR-CONTAINING ADDITIVES WITH METALS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 4, 1980 pp 31-32

NOVITSKAYA, G. N., LEBEDEV, Ye. V. and SARNAVSKAYA, T. I., VNIIPKneftekhim

[Abstract] The chemical activity of sulfur-containing anti-oxidation metal additives, as represented by heterocyclic compounds with various position and content of sulfur atoms in the molecule (3-phenyl-5-ethyl-4-thionethiazolidone-2(I), dimorpholydi-(II) and dimorpholyltetrasulfide (III)), was investigated by means of differential-thermal and x-ray diffraction analysis, in the presence of chemically pure hydrogen-reduced iron as well as electrolytic copper. At 150°C the products of the thermodestruction of (I) undergo chemical interaction with copper and the oxygen of the air. The products of that interaction are  $\text{Cu}_2\text{O}$  and the copper sulfides  $\text{Cu}_{1.96}\text{S}$  and  $\text{CuS} \cdot 4\text{Cu}_2\text{S}$ .

Chemically pure iron does not interact with (I) at that temperature. As for compound (III), in which--unlike in compound (I)--the sulfur atoms are located outside the cycle, chemical interaction with copper commences already at 100°C, with the formation of  $\text{CuS}$ ,  $\text{CuSO}_4$ ,  $\text{Cu}_{1.96}\text{S}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_{1.765}\text{S}$ , and  $\text{CuO}$ . The presence of a compound of the  $\text{CuS} \cdot 4\text{Cu}_2\text{S}$  type was also established. The remainder is pure copper. Compound (II) is characterized by an interaction of a different type, resulting in the formation of  $\text{CuS}_4$ . Since some of the diffraction maxima for the compounds  $\text{CuS}$ ,  $\text{Cu}_{1.96}\text{S}$ ,  $\text{CuO}$ , and  $\text{Cu}_2\text{O}$  display the same interplanar spacing, an unambiguous determination of the quantitative proportions of the investigated products is difficult. Nevertheless, the findings of x-ray diffraction analysis offer a valuable complement to the findings of differential-thermal analysis and serve to elucidate the phase composition of the products of interaction of the additives and metals. Figures 2; references 8: 4 Russian, 4 Western.

[162-1386]

ALL-UNION CONFERENCE ON CHEMISTRY AND TECHNOLOGY OF PRODUCTION OF LIQUID AND GASEOUS FUEL FROM COAL, SHALE AND PETROLEUM RESIDUES (26-28 Sep 79, Zvenigorod)

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 60-61

KRICHKO, A. A.

[Abstract] The 252 persons representing 87 organizations at the conference presented 44 papers and 45 addresses on aspects of the present state of scientific research, experimental design and industrial operations in synthetic fuels production. Emphasis was placed on the vast coal supplies in the eastern USSR (90% of the national supply) which must be considered in development of mining and engineering problems involving the working of it. The brown coals of Kask-Achinsk Basin and the bituminous coal from Kuznetsk Basin were discussed as the basis of future production. A specific program of studies in the area of synthetic fuels production was developed at the conference, with recommendation that this program be completed in the first half of 1980. Institutional organizational plans related to the problems of the conference were also discussed.  
[182-2791]

UDC 665.7.038/64

#### MANNICH'S BASE AS AN ANTI-OXIDANT ADDITIVE TO JET FUELS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 39-42

VISHNYAKOVA, T. P., GOLUBEVA, I. A., GUTNIKOV, L. P., SEREGIN, Ye. P., PROKUDIN, V. N., and VESELYANSKAYA, V. M.

[Abstract] A study of 4-(N,N-dimethylaminomethylene)-2,6-di-tertiary-butylphenol (Mannich's base) and compositions based on it showed it to be an effective anti-oxidant additive for jet fuels. In addition to being as effective as ionol, it was found to be less expensive and to have the capacity to inhibit developing processes of oxidation. The most effective of the compositions studied was Mannich's base with isopropylphenyl-n-phenyldiamine (4010NA). This additive and compositions based on it should be more widely tested. References 4; Figures 2.  
[182-2791]

UDC 665.754:662.742

#### ENERGY SUPPLY TO PETROLEUM PROCESSING PLANTS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 29-31

DERBAREMDIKER, M. I., KIRICHENKO, N. A., NIKOLAYEV, N. I., and YERMAKOV, V. G.

[Abstract] A process of gasification of petroleum residues and purification of the gas which converts the chemical energy of the fuel into chemical and mechanical energy of the compressed gas and energy of the water vapor provides fuel savings of up to 8% due to use of mechanical energy of the compressed gas in the gas turbine, reduction of heat loss with smoke, and reduction of SO<sub>2</sub> content in the smoke. References 3; figure 1.  
[182-2791]

UDC 547.461.4:547.415.5

#### SUCCINIMIDE ADDITIVES BASED ON C<sub>18</sub> - C<sub>40</sub> FRACTIONS OF PRODUCTS OF HIGH TEMPERATURE OLIGOMERIZATION OF ETHYLENE

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 24-27

OSTROVERKHOV, V. G., GLAVATI, O. L., CHERMENIN, A. P., RABINOVICH, I. L. and DETS, M. M.

[Abstract] Succinimide additives were prepared on an alpha-olefins base with diethylenetriamine (DETA) at a molar ratio of alkenylsuccinic acid: DETA = 1 : 0.55 and 1 : 1 (sample A and B) and an analogous additive B was prepared on the base of alpha-olefins residue from vacuum distillation of C<sub>18</sub> - C<sub>40</sub> fractions. Laboratory studies and studies in Petter W-1 and Petter AV-1 engines of the detergent-dispersing and other functional properties of these additions in oils M-11, M6Z/10G and MBV, showed them to equal the commercial succinimide additive S-5A while their functional properties equalled those of additives based on products of low-temperature oligomerization of ethylene. Oil with additive B while less effective in detergent-dispersing properties, reduced lead corrosion and the inclination to low-temperature slurry formation. References 5.  
[182-2791]

## THE EFFECT OF CONCENTRATION OF ANTI-ABRASION AND ANTI-SCRATCH ADDITIVES ON THEIR EFFECTIVENESS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 21-23

ZASKAL'KO, P., GUREYEV, A. A., MUMINDZHANOV, N. M., and CHECHETKIN, V. V.

[Abstract] Additives containing active elements S, P and N (Anglamol-99, Khaytek E300; S and Cl (PZ-28); S(LZ-23k, IKhP-14, ABES and OTP); Cl and P (Khlorek-40); S, Cl and P (LZ-309/2); S, P and CA (MNI-IP22k) were studied. Medicinal liquid petrolatum served as the base oil (carrier of the additive) in these studies. It was found that their anti-abrasion and anti-scratch effectiveness depend upon their structure and their concentration in the oil. A classification of the additives according to their functional properties was proposed. References 3; figures 3. [182-2791]

## RESORCINOL ALKYLDERIVATIVES AS ANTI-OXIDANT ADDITIVES TO JET FUEL

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 18-21

LYKOV, O. P., VISHNYAKOVA, T. P., TUMAR, N. V., SEREGIN, E. P., PROKUDIN, V. N., and KONISHCHEVA, I. A., Moscow Institute of the Petrochemical and Gas Industry imeni Academician I. M. Gikkin

[Abstract] A study of the effect of resorcinol alkyl derivatives and other bivalent phenols on the thermal stability of jet fuels (T-6, T-7, PT, T-8B) produced by hydrogenation processes showed these derivatives to be effective anti-oxidant additives for such fuels. They do not impair the operational properties of the fuel and greatly improve the antiwear properties of fuel T-7. References 6; figures 2. [182-2791]

## AMINODISULFIDES AS ADDITIVES TO LUBRICANTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 10-11

BALIN, A. I., VERETENOVA, T. N., and TARASEVICH, V. B., All-Union Scientific Research Institute of Polycarbonates Petrochemistry

[Abstract] Study and development of a technology of production of sulfur and nitrogen containing additives of the aminodisulfide type by means of interaction of beta, beta-dichlorodialkyl (aryl) disulfides with diethanolamine in the medium of a solvent--diethanolamine was described. The 2,2-bis-(diethanol) dialkyl (aryl) disulfides produced are not hydrolyzed in aqueous solutions of the alkalies, possess rather high anti-abrasive properties and are recommended for tests as active additives to lubricating-cooling fluids and oil and emulsion type industrial lubricants. References 4.

[182-2791]

## PRODUCTION OF ARCTIC DIESEL FUEL WITH A DEPRESSOR ADDITIVE

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 5-7

POMOLOVSKIY, L. A., ENGLIN, B. A., VERETENNIKOVA, T. N., NIKOLAYEVA, V. G., and SINITSYNA, G. D., All-Union Scientific Research Institute of the Petroleum Industry

[Abstract] The possibility of producing arctic diesel fuel with solidification point no higher than  $-60^{\circ}\text{C}$  based on straight run diesel fuel with cetane number 46, solidification point  $-55^{\circ}\text{C}$  and cloud point  $-32^{\circ}\text{C}$ , obtained from Eastern paraffin petroleum was studied. Production of such fuel was found to be possible on the base of diesel fractions of light fractional composition by the addition of 0.01-0.05 percent PMA'd additive (a polymer type additive based on ethers of metacrylic acid). References 3; figure 1.

[182-2791]

## MODELLING HYDROCRACKING OF THE HEAVY GASOLINE FRACTION

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 5, 1980 signed to press 24 Mar 80 pp 3-5

ZHOROV, Yu. M., PANCHENKOV, G. M., TAMARIBITSEVA, G. M., KHAVKIN, V. A., KOZLOV, I. T., and AGAFONOV, A. V.

[Abstract] A chemical scheme of hydrocracking of heavy gasoline fractions to produce considerable amounts of isobutane and isopentanes was developed and its mathematical description and results of modelling it were presented. Results of the use of the procedure for calculating the composition of products of hydrocracking of individual hydrocarbons were also presented. Optimal conditions of production of isoparaffin hydrocarbons  $C_4 - C_6$  from the gasoline fractions were determined on the basis of the mathematical model. References 6.  
[182-2791]

## INVESTIGATION OF THE STRUCTURE-GROUP COMPOSITION OF HIGH-BOILING FRACTIONS OF THE LIQUID PRODUCTS OF PYROLYSIS BY MEANS OF PMR- AND IR-SPECTROSCOPY

Moscow NEFTEKHIMIYA in Russian No 1, 1980 pp 136-141 manuscript received 15 Feb 79

KURASHEV, M. V., KOSHEVNIK, A. Yu., TRUKHMANOVA, N. I., MASHIN, V. N. and BERENTZ, A. D., Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences

[Abstract] The high-temperature pyrolysis of crude with the object of producing ethylene results in the formation of a large quantity of liquid products (pyrolysis tars boiling out at above  $200^{\circ}\text{C}$ ) containing valuable mono- and polycyclic hydrocarbons. The quantitative characteristics of their hydrocarbon composition can be determined only by a combination of techniques rather than by a single technique. Accordingly, both PMR- and IR-spectroscopic methods were used to investigate the structure-group composition of the high-boiling liquid products of pyrolysis of gas-condensate gasoline. The narrow high-boiling cuts obtained upon rectification (11 cuts, boiling out at from  $>200^{\circ}\text{C}$  to  $520^{\circ}\text{C}$ ) were examined for molecular mass and IR and PMR spectra. The investigated cuts, and especially their aromatic

parts, are generally characterized by a low mean molecular mass, and at least 80-95% of their content consists of aromatic hydrocarbons with 1-4 benzene rings and alkyl or naphthene substituents. In general, the content of methyl groups in the fractions decreases with increase in the b.p. of the fraction. The mean content of methine and methylene groups in the paraffinic-naphthenic part of high-boiling fractions has also been calculated, and the composition of that part can be assumed to correspond to the formula  $C_nH_{2n}$ , which may be represented by a molecule consisting of one naphthene ring with a number of alkyl substituents. References 8: 1 Russian, 7 Western.  
[149-1386]

UDC 661.719.2

#### INTERACTION OF MERCAPTANS WITH CYCLOHEXENE

Moscow NEFTEKHIMIYA in Russian No 1, 1980 pp 127-130 manuscript received 19 Sep 78

GADZHIYEV, M. K., NEBIYERIDZE, N. M. and ARESHIDZE, Kh. I., Institute of Physical and Organic Chemistry imeni P. G. Melikishvili, Georgian SSR Academy of Sciences

[Abstract] Interaction of mercaptans of the aliphatic series with cyclohexenes was investigated in a nitrogen atmosphere in the presence of shards of glass. The mercaptans (ethanethiol, n-propanethiol-1, isopropanethiol, n-butanethiol-1, n-pentanethiol-1) were reacted with cyclohexene at from 160 to 240°C as well as at mass flow rates of from 0.25 to 1.0 hr<sup>-1</sup> and at molar ratios of 0.5-2:1. The actual yields of ethyl-, n-propyl-, isopropyl-, n-butyl-, and n-amylocyclohexylsulfides were 97.5, 94.7, 95.2, 92.3, and 90.1 mass%, respectively. For ethanethiol the optimal conditions of reaction with cyclohexene were: 180°C, molar ratio 1.5:1, mass flow rate 0.5 hr<sup>-1</sup>. For n-propanethiol, isopropanethiol, n-butanethiol-1, n-pentanethiol-1 the corresponding optimal conditions of reaction with cyclohexene were 200, 200, 210, and 270°C, respectively for the molar ratio 1.5:1 and mass flow rate 0.5 hr<sup>-1</sup>. These findings should broaden the range of known techniques for synthesizing the alkylcyclohexylsulfides present in crude. Figure 1; references 5: 4 Russian, 1 Western.  
[149-1386]

## SYNTHESIS OF PHTHALIC ANHYDRIDE FROM THE NAPHTHALENE OF PYROLYSIS TAR

Moscow NEFTEKHIMIYA in Russian No 1, 1980 pp 115-121 manuscript received 13 Oct 78

ALEKSEYEVA, T. A. and IL'IN, V. A., Uralkhimplast Ural Chemicals and Plastics Production Association

[Abstract] Samples of naphthalene isolated from the naphthalene fraction of pyrolysis tars were investigated as a potential raw material for expanding the production of phthalic anhydride. Compared with standard naphthalene (I) produced as a byproduct of the coke industry (~7.5% impurities), the naphthalene obtained from pyrolysis tars (II) proved to contain 2-4% impurities. However, the yield of phthalic anhydride from naphthalene (I) is greater than from (II). Tests of spent catalyst revealed a lower sulfur content and degree of oxidation for naphthalene (II); the lower sulfur content may be due to the insufficient sulfur content of the oxidized naphthalene. Experiments indicate that the performance of the catalyst can be improved if it is continually regenerated with a sulfur compound such as sulfurous acid anhydride; then the composition of products (phthalic anhydride, maleic anhydride, 1,4-naphthoquinone, etc.) from naphthalene II becomes identical with that of naphthalene I. References: 8 Russian. [149-1386]

## SYNTHESIS OF CARBOXYLIC ACIDS THROUGH OXIDATION OF MIDDLE FRACTIONS OF CRUDE

Moscow NEFTEKHIMIYA in Russian No 1, 1980 pp 101-107 manuscript received 5 Feb 79

SZALAJKO, U., FISZER, S. and PADOWICZ, E., Gliwice, Polish People's Republic, Silesian Polytechnical Institute

[Abstract] The possibility of oxidative synthesis of aliphatic mono- and dicarboxylic acids from the middle fractions of paraffin-free crude was investigated. The oxidation of the middle fractions (boiling range 200-350°C; with the aromatic hydrocarbons removed; composition--practically only naphthenic (40%) and isoparaffinic (60%) hydrocarbons) was performed at 120-150°C on using nitrogen oxides as the catalyst. A mathematical model of the oxidative process was constructed on the basis of regression formulas. The

naphthenic acids thus synthesized were found to differ from natural naphthenic acids by having a high content of polyfunctional oxygen-containing compounds of an acid nature that are insoluble in light petroleum and that can be oxidized into dicarboxylic acids. This finding is of special interest considering that these poly-acids form under the above conditions in quantities much greater than those yielded by the analogous oxidation of liquid alkanes isolated upon reaction with carbamide. Figures 4; references 6: 3 Russian, 2 Polish, 1 Western.  
[149-1386]

UDC 547.537:542.97

#### TRANSFORMATIONS OF PHENYL- AND BENZYL CYCLOBUTANES IN THE PRESENCE OF $AlBr_3$

Moscow NEFTKhimiya in Russian No 1, 1980 pp 75-81 manuscript received 4 May 79

FINKEL'SHTEYN, Ye. Sh., MIKAYA, A. I., ZAIKIN, V. G. and VDOVIN, V. M.,  
Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences

[Abstract] The directions of transformations of phenyl- (I) and benzylcyclobutanes (II) in the presence of the catalyst  $AlBr_3$  were investigated. The reactions were performed in vacuum glass ampoules filled with phenyl- (or benzyl-) cycloalkane, n-nonane (internal standard), benzene, and  $AlBr_3$  in the molar ratio 1:1:10:0.2. It was found that, in the presence of  $AlBr_3$ , (I) undergoes skeletal isomerization into 1-methylindane and tetraline as well as hydrodehydrogenation with the formation of 2-phenyl- and 1-phenylbutanes and disproportionation with the formation of dicyclobutylbenzenes. Contact with  $AlBr_3$  causes (II) to undergo isomerization into 2-methyltetraline and phenylcyclopentane. The final mixture also contained a hydrogen disproportionation product--1-phenyl-2-methylbutane. A comparative study of the homologues of (I) and (II) under the same conditions--phenylcyclopentane (III), benzylcyclopentane (IV) and phenylcyclohexane (V) revealed that these homologues are incapable of getting isomerized into condensed bicyclic structures. Thus, in the series investigated, skeletal isomerization into bicyclic structures of indane and tetraline type is a property only of the aromatic derivatives of cyclobutane. It was also found that all the investigated phenylcycloalkanes ( $C_4$ ,  $C_5$ ,  $C_6$ ) undergo disproportionation of the cycloalkyl groups. References 18: 14 Russian, 4 Western.  
[149-1386]

# ALKYLATION OF BENZENE WITH DECENE IN THE PRESENCE OF THE CATALYTIC SYSTEM $AlR_{3-n}Cl_n \cdot TiCl_4 \cdot RX$

Moscow NEFTEKHIMIYA in Russian No 1, 1980 pp 71-74 manuscript received 20 Jun 79

BUSHEVA, Z. G., GOLUBEV, V. K. and POLACHEVA, A. I.

[Abstract] The alkylation of benzene by means of higher alpha-olefins with the aid of the catalytic system  $AlR_{3-n}Cl_n \cdot TiCl_4 \cdot D$  (where D is an alkylhalide and the first two components of that system catalyze the oligomerization of ethylene in a benzene solution) was investigated. The reactants (benzene, decene, octyl chloride) were previously dried on NaA zeolite and distilled. The reaction products were analyzed with the aid of a Tavet-2 chromatograph. It was found that the composition of the products of alkylation performed with the aid of the catalytic system  $Al(C_2H_5)_{1.5}(Cl_{1.5} \cdot TiCl_4 \cdot alkylhalide)$  depends on the molar ratio between the alkylhalide and the alkylaluminumhalide. Increasing the molar ratio  $RX:Al$  from 0.25:1 to 1.5:1 increases the yield of monoalkylbenzene to 85-86 wt.% of the total amount of alkyl derivatives. References: 10 Russian. [149-1386]

# ISOMERIZATION OF m-XYLENE ON CATION-EXCHANGE FORMS OF SILICA-ALUMINA CATALYST

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YEGIAZAROV, Yu. G., SAVCHITS, M. F., POTAPOVA, L. L. and ROMANOVSKIY, B. V., Institute of Physico-Organic Chemistry, Belorussian SSR Academy of Sciences; Moscow State University ineni M. V. Lomonosov

[Abstract] The effect of exchange cations on the acid properties of silica-alumina catalyst (SAC) was investigated with respect to the isomerization of m-xylene at 450°C. SAC specimens with the cations  $Al^{3+}$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  were calcined at 485°C in argon prior to the delivery of m-xylene to the reaction vessel. The reaction products were analyzed with a Khrom-31 chromatograph. It was found that, on the investigated catalysts, m-xylene is transformed into o- and p-xylenes as well as into disproportionation

products. The catalytic activity of the various cation-exchange forms of SAC was found to be in a correlation with their relative acidity. The isomerization of *m*-xylene with the aid of alkali-earth cation-exchange forms of SAC gets promoted by small quantities of H<sub>2</sub>O, apparently because the formation of hydroxyl groups in zeolites containing polyvalent ions involves the dissociation of the water molecule under the action of the electrostatic field of the cation. Heat treatment of the zeolites, on the other hand, results in the converse reaction of the dehydroxylation of polyvalent cations. On the whole, the Mg form of SAC appears to be the most promising, since then stable yields of *n*-xylene exceed 20% and the selectivity remains sufficiently high (85-87%). Figures 2; references 10: 6 Russian, 4 Western.  
[149-1386]

UDC 553.982:[543.51+543.544]

#### HYDROCARBON COMPOSITION OF THE MIDDLE FRACTIONS OF CRUDES IN THE PERMIAN DEPOSITS OF TATARIYA

Moscow NEPTEKHIMIYA in Russian No 1, 1980 pp 20-25 manuscript received 26 Dec 77

KURBSKIY, G. P., KAYUKOVA, G. P. and YEFREMOV, Yu. Ya., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch of the USSR Academy of Sciences

[Abstract] The hydrocarbon composition of middle fractions of 6 Tatar crudes from various strata of the Permian system was investigated by mass-spectrometric and gas-chromatographic techniques. They were found to display a high density (0.95-1.02) and viscosity as well as a high total sulfur content (2.8-4.4%), tars, and asphaltenes, but their physicochemical properties varied broadly regardless of the depth of the strata. These variations may be attributed to differences in the intensity of the effect of hypergenesis factors. These middle fractions moreover contain little or no *n*-paraffin hydrocarbons, apparently owing to progressive destruction of these hydrocarbons by bacteria in Permian deposits. All the crudes investigated contain isoprenoid hydrocarbons of C<sub>14</sub>-C<sub>20</sub> composition. The heavier the crude the lower its content of isoprenoid hydrocarbons with lower molecular weight, and the more likely it is not to contain *n*-paraffin hydrocarbons. The heavier crudes also contain higher proportions of mono- and bicyclic naphthenes. The aromatic hydrocarbons of the middle fractions consists 28-37% of alkyl benzenes. All the crudes contain benzthiophene structures. Figure 1; references 12: 8 Russian, 4 Western.  
[149-1386]

## THERMAL DISSOLUTION OF BALTIC SEABOARD SHALES IN A UNIFLOW FACILITY

Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 2, 1980 pp 67-70 manuscript received 10 Jul 79

VOL'-EPSHTEYN, A. B., SHPIL'BERG, M. B. and BREGADZE, T. A., Institute of Fossil Fuels

[Abstract] Shales are normally dissolved under a pressure of 30-50 atm in a solvent at 400-430°C in order to obtain the principal product--heavy oil, along with gasoline and the regenerated solvent. In this connection, the thermal dissolution of Baltic shale in a uniflow facility with separation of liquid products of the process by distillation was experimentally investigated using the fraction with b.p. of 210-340°C as the solvent. The experiments were performed under a pressure of 50 atm and at 400-440°C in a laboratory uniflow setup with a reactor having a volume of 3 liters on using a shale-to-solvent ratio of 1:1.3. A diagram of the uniflow setup is presented. The solubility of the organic mass of the shale, i.e., its conversion to liquid and gaseous products, was 90%. The results showed promise, so that plans exist to build a pilot facility (capacity 5,000 tons of concentrated shale annually) at the Slantsy Shale Processing Plant. Figure 1; references: 3 Russian.  
[147-1386]

## EFFICIENT UTILIZATION OF HEAVY PYROLYSIS RESINS

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 289-296 manuscript received 10 Nov 78

FRYAZINOV, V. V., KOLESNIKOVA, T. A., MUKHINA, T. N., TSEKHANOVICH, M. S., YEZHOV, B. M., LESOKHINA, G. F., and SLUTSKAYA, S. M., Bashkir Scientific Research Institute on Petroleum Refining, All-Union Scientific Research Institute of Organic Synthesis and All-Union Scientific Research Institute of Commercial Carbon

[Abstract] The composition of heavy residues from liquid pyrolysis products of different types of raw material was studied. The raw material was characterized by high content of coke-forming components such as polycyclic aromatic hydrocarbons, resins and asphaltenes and low sulphur content. The

use of heavy pyrolysis resins in coking in a mixture with cracking residues and crude asphalt from sour oil in ratios of 40:60 and 30:70 permits a reduction of sulphur content in the coke from 1.9-2.3 to 1.4-1.5 percent. The yield of coke for the mixed coking raw material is increased and the metal impurity content in it is significantly reduced. Coke with sulphur content from 0.08 to 1.48 percent can be produced when pyrolysis resin is coked in pure form as a function of the type of pyrolysis raw material. The light and medium fractions of the distillates produced in coking pyrolysis resins can be utilized to extract aromatic hydrocarbons and naphthalene and the heavy fractions can be used as a raw material for commercial carbon with correlation index of 120-130. References 6: 4 Russian, 2 Western.  
[184-6521]

UDC 547.57.541.127

#### LIQUID-PHASE OXIDATION OF TETRAHYDROBENZALDEHYDE BY MOLECULAR OXYGEN

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 268-272 manuscript received 30 Mar 79

NOVAK, A. M., KUCHER, R. V., OPEYDA, I. A. and BATOG, A. Ye., Institute of Physical-Organic Chemistry and Organic Chemistry of the Ukrainian SSR Academy of Sciences, Donetsk

[Abstract] The kinetic principles of liquid-phase oxidation of tetrahydrobenzaldehyde by molecular oxygen were investigated and the possibility of producing a number of oxygen-containing compounds based on tetrahydrobenzaldehyde was determined. The tetrahydrobenzaldehyde was oxidized on a gasometric installation, using the same experimental technique as in benzaldehyde oxidation. The experiment was conducted at oxygen pressure of 0.1 MPa and at temperature of 75° in chlorobenzene. The effective activation energy of the oxidation reaction and the order of the reaction by aldehyde and oxygen were determined. Peroxides, acids and epoxy compounds are formed during oxidation of tetrahydrobenzaldehyde. A simplified scheme of the proposed mechanism of the oxidation reaction is proposed. Solvents have a significant effect on the process of tetrahydrobenzaldehyde oxidation. Figures 2; references 9: 8 Russian, 1 Western.  
[184-6521]

## REACTION OF 1,3-DIOXACYCLANES WITH CUMYLPEROXYRADICALS

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ESTRINA, G. Ya., AGISHEVA, S. A., KURAMSHIN, E. M., IMASHEV, U. B., ZLOTSKIY, S. S., and RAKHMANKULOV, D. L., Ufa Petroleum Institute

[Abstract] The activity of 1,3-dioxacyclanes in reaction with cumylperoxy-radicals was determined and the effect of the dimensions of the ring and the position of the substituents on the reactivity of these compounds were followed. The rates and rate constants of the interaction of cumylperoxy-radicals with a number of cyclic acetals were measured and calculated. The acetals were oxidized in a chlorobenzene solution in the presence of an initiator of dinitrile azoisobutyric acid and cumylhydroperoxide. The cumylhydroperoxide was introduced in a concentration which provided total replacement of the peroxide radicals of the substrate by the cumylperoxyradicals. The activity of unsubstituted and substituted acetals decreases in the series 1,3-dioxolane > 1,3-dioxane > 1,3-dioxepane. The alkyl groups of the C(2) atom reduce the reactivity of acetals and the substitutes of C(4) and C(5) atoms slightly alter the activity. Figures 1; references 10: 6 Russian, 4 Western.  
[184-6521]

## LIQUID-PHASE OXIDATION OF PHENYLCYCLOPENTANE AND PRODUCTION OF PHENYLCYCLOPENTANE HYDROPEROXIDE

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 260-263 manuscript received 9 Apr 79

KOSHEL', G. N., GLAZYRINA, I. I., MYTSYK, N. P., and FARBEROV, M. I., Yaroslavl' Polytechnical Institute

[Abstract] Selective production of phenylcyclopentane hydroperoxide by liquid-phase oxidation was studied as one of the stages of joint production of phenyl and cyclopentane. Liquid-phase oxidation of phenylcyclopentane was carried out at 100-125°C in the presence of phenylcyclopentane hydroperoxide initiator in the amount of one percent by mass. The average rate of hydroperoxide accumulation increases from 3.5 to 25 percent/hr by mass as the oxidation temperature increases from 100 to 125°. The selectivity of the reaction depends on hydrocarbon conversion and it decreases with an

increase of hydrocarbons. The rate of phenylcyclopentane oxidation exceeds approximately fivefold the rate of phenylcyclohexane oxidation from comparison of data on liquid-phase oxidation of phenylcyclopentane and phenylcyclohexane. The rate constants of continuation of the chain for phenylcyclopentane and phenylcyclohexane oxidation were calculated. These two compounds have essentially the same thermal stability, as indicated by study of thermal breakdown of hydroperoxides of these hydrocarbons. Figures 1; references 14: 11 Russian, 3 Western.  
[184-6521]

UDC 547.534.1:542.943.7

#### THE JOINT EFFECT OF COPPER NAPHTHENATE AND DITRIOPHOSPHATES OF METALS UPON OXIDATION OF ETHYLBENZENE

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 252-259 manuscript received 1 Jun 78

IVANOV, S. K. and BONEVA, M. I., Institute of Organic Chemistry of the Bulgarian Academy of Sciences, Sofia

[Abstract] The kinetics of liquid-phase oxidation of ethylbenzene in the presence of copper naphthenate alone and with joint action with zinc diisopropyldithiophosphate were investigated. The naphthenate concentration, water formed, temperature, air flow rate and the presence of acetophenone affect the oxidation process in oxidation of ethylbenzene in the presence of cobalt naphthenate. The oxidation of ethylbenzene proceeds selectively with production of acetophenone. Lesser quantities of benzoic acid and methylphenylcarbonyl are formed, while no styrene is formed. Copper naphthenate increases the liquid-phase oxidation of ethylbenzene due to interaction between the catalyst and inhibitor. The use of copper naphthenate to intensify the oxidation of lubricating oils is feasible only in the absence of metal-complex sulphur and phosphorus-containing compounds. Figures 3; references 22: 10 Russian, 12 Western.  
[184-6521]

# OXIDATION OF CUMENE BY AN OZONE-OXYGEN MIXTURE

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 245-251 manuscript received 25 Jan 78

SHERESHNEVETS, V. V., KOMUSSAROV, V. D., and DENISOV, Ye. T., Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Division of the Institute of Chemical Physics of the USSR Academy of Sciences

[Abstract] The mechanism of ozone initiation reaction, the effectiveness of initiation and the ratio between the rate constants of the ozone flow rate in the reaction to the lateral chain and the aromatic nucleus were studied. The role of ozone in reactions of chain continuation and the effect of the process on the composition of the formed products were determined. The mechanism of the process, according to which ozone is consumed only during the primary reaction with cumene, forming ozonides, dimethylphenylcarbynol and free radicals, is proposed as a result of studying the kinetic principles and composition of the products of cumene oxidation by an ozone-oxygen mixture at 25 and 65°C. The composition of the reaction products depends on the ozone content in the ozone-oxygen mixture. The yield of hydroperoxide decreases and the yield of dimethylphenylcarbynol increases sharply with an increase of ozone concentration. Figures 3; references 20: 10 Russian, 10 Western. [184-6521]

UDC 661.183.6:665.656

# HYDROISOMERIZATION OF DIESEL FUEL ON MODIFIED PALLADIC ZEOLITE-CONTAINING CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 237-241 manuscript received 16 Nov 78

SHARIKHINA, M. A., DYRIN, V. G., LOGINOVA, A. N., LEVINTER, M. Ye., and BAKULIN, R. A., Kuybyshev Polytechnical Institute imeni V. V. Kuybyshev

[Abstract] Several specimens of palladic zeolite-containing catalysts were synthesized and tested on a flow-through laboratory installation under hydrogen pressure of 3 MPa, volumetric feed rate of 1.2 hr<sup>-1</sup> and volumetric hydrogen to raw material ratio of 1,000:1 in the temperature range of 340-380°. Diesel fuel made from Mangyshlak oil was used as the raw material.

Three series of palladic zeolite-containing catalysts were prepared. The catalysts of the first series were distinguished by the degree of sodium exchange, those of the second series were distinguished by a silicate modulus varied by changing the multiplicity factor of processing the initial zeolite by a hydrochloric acid solution, and the catalysts of the third series were represented by quintuple dealuminized H-mordenite modified by calcium and magnesium cations. The catalysts produced on the basis of dealumination of zeolites have higher acidity and higher activity compared to those produced on the basis of decationized zeolite. The addition of calcium or magnesium cations to the catalysts intensifies the catalytic activity. The use of catalysts produced on the basis of dealuminated mordenite and modified by additional introduction of magnesium cations makes it possible to produce diesel fuel from Mangyshlak oil with congealing temperature below  $-35^{\circ}\text{C}$ . Figure 1; references: 7 Russian. [184-6521]

UDC 547.562.1:66.095.253

#### CHARACTERISTICS OF PHENOL ALKYLATION BY MEANS OF OLEFINS ON MACROPOROUS CATION EXCHANGERS

Moscow NEFTKHIIMIYA in Russian Vol 20, No 2, 1980 pp 208-211 manuscript received 17 May 79

SEKHOVERKHOVA, L. V., CHEREDNICHENKO, G. I., GORDASH, Yu. T., ZHURBA, A. S., SEKHOVERKHUV, V. D., and FEDORENKO, L. G., All-Union Scientific Research and Planning-Design Institute of the Petroleum Refining and Petrochemical Industry, Kiev

[Abstract] The volumetric changes of gel and macroporous cation exchangers dried by different methods and subjected to swelling in water and phenol were compared. Microphotographs were taken of the cation exchanger granules in the working state. The high strength of macroporous cation exchanger and appreciably fewer volumetric changes compared to the gel type are indicated. KU-23 macroporous sulfocation exchanger does not break down upon drying and swelling in phenol as does KU-2-8 gel. The volumetric changes of KU-23 cation exchanger grains are considerably less upon swelling in water and phenol than those of KU-2-8 cation exchanger. The use of macroporous KU-23 cation exchanger as a catalyst for phenol alkylation by olefins permits a 2.5-3-fold increase of the volumetric rate of the raw material when compared to similar alkylation on KU-2-8 gel cation exchanger. Figures 2; references: 8 Russian. [184-6521]

## EQUILIBRIUM COMPOSITION AND PROPERTIES OF EPIMERS OF REARRANGED CHOLESTANE

Moscow NEFTEKHIMIYA in Russian Vol 20, No 2, 1980 pp 183-193 manuscript received 26 Apr 79

KAYUKOVA, G. P., PUSTIL'NIKOVA, S. D., ABRYUTINA, N. N., GOLOVKINA, L. S., and PETROV, A. A., Institute of Geology and Exploitation of Fuel Minerals

[Abstract] The compound  $5\beta\text{CH}_3$ , 14  $\text{CH}_3$ -dimethyl-18,19-dinor-8aH, 9aH, 10aH- $\Delta^{13-17}$ -cholestene was synthesized and a mixture of epimers of rearranged cholestane was produced by subsequent hydrogenation. A total of 12 diastereomers with different configuration were identified as a result. An equilibrium mixture of the epimers was produced by configurational isomerization at 570 K in the presence of platinized carbon. The predominant components under equilibrium conditions were two epimers having 10aH, 13aH, 17aH (20R and 20S)-configuration which comprises more than 50 percent of the entire equilibrium mixture. Epimers having 10aH, 13aH, 17aH- and 10aH, 13aH, 17aH-configuration are also present in lower concentrations. The mass spectra and the relative holding times of the 12 identified diastereomers of rearranged cholestane were determined. Figures 2; references 9: 3 Russian, 6 Western.  
[184-6521]

UDC 621.892.099.21:65.018

## PERFORMANCE OF THE C AND D GROUPS OF MOTOR OILS

Moscow KHMIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, 1980 pp 22-24

SINYANSKAYA, R. I., VOL'NYKH, V. I., and SHUMKOVA, Ye. V., et al

[Abstract] Group D motor oils were developed for heavy Diesel engines. Their performance was compared with group C oils on a tractor engine, ADVT-30, under laboratory conditions. The tests showed that the low ash containing oil M-10DM was the best; after running for 240 hours, it showed the highest reserves of detergent, neutralizing and stabilizing properties, and an adequate dispersive ability. This oil should be effective in engines even after 240 hours of operation, assuring the lowest wear and tear on the motors' parts. References: 2 Russian.  
[150-7813]

## CATALYTIC CRACKING OF VACUUM GAS-OIL FROM MANGYSHLAK PETROLEUM OVER ZEOLITE CONTAINING CATALYSTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, 1980 pp 8-11

SOSKINO, D. M., SAMOYLOVA, N. N., and VORONOVA, O. K., et al

[Abstract] In connection with the conversion of the equipment to zeolite containing catalyst, pilot plant cracking experiments were carried out with vacuum gas-oil (350-500°C) from Mangyshlak petroleum using a moving catalyst layer. Experiments were also carried out in a laboratory setup with a stationary pseudoliquefied catalyst layer. The effect of three factors on kinetic process was studied: temperature, the rate of crude oil input and the ratio of the catalyst to crude oil. The yield of gasoline as a function of the temperature and the rate of the material input was reported graphically for the catalyst:crude ratio of 6 (optimal). Also, the yield of cracking products, percent conversion and the octane number were reported as functions of the reaction temperature. The temperature was found to be the principal factor controlling gasoline properties (yield, octane number, production of coke and gas, etc.). Figures 3; references: 2 Russian.

[150-7813]

## SULFOACIDS FORMED DURING SULFURIC ANHYDRIDE SULFONATION OF BASIC OILS FROM WEST SIBERIAN PETROLEUM

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, 1980 pp 40-43

POTOLOVSKIY, L. A., KATRENKO, T. I., and POLYAKOVA, A. A., et al, All-Union Scientific Research Institute of Petroleum Reprocessing

[Abstract] During sulfonation of petroleum basic oils, sulfoacids comprised of various derivatives of aromatic and naphtheno-aromatic hydrocarbons, are formed. There are three basic groups of these acids: water soluble, oil soluble and oil insoluble; their chemical structure is unknown. Oil soluble sulfoacids are soluble in oils and various organic solvents; in water they are either soluble or practically insoluble. In the sulfonation of the residual oil and of the DC-14 oil, all three sulfoacid groups are formed, with the majority of them being oil soluble. The oil soluble

sulfoacids show lowest acid number and highest molecular weight. By means of mass-spectrometry, seven types of oil soluble monosulfoacids have been identified. The results of these studies are very important in the development of the synthesis and technology of sulfonate additives. References 12: 11 Russian, 1 Western.  
[150-7813]

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